

May be used only for educational or research purposes.

Bonança, Marcus V. S. and Sebastian Deffner. "Fluctuation theorem for irreversible entropy production in electrical conduction." Phys. Rev. E 105, L012105 (24 January 2022).
<https://doi.org/10.1103/PhysRevE.105.L012105>

Access to this work was provided by the University of Maryland, Baltimore County (UMBC) ScholarWorks@UMBC digital repository on the Maryland Shared Open Access (MD-SOAR) platform.

Please provide feedback

Please support the ScholarWorks@UMBC repository by emailing scholarworks-group@umbc.edu and telling us what having access to this work means to you and why it's important to you. Thank you.

Fluctuation theorem for irreversible entropy production in electrical conductionMarcus V. S. Bonança^{1,*} and Sebastian Deffner^{2,1,†}¹*Instituto de Física “Gleb Wataghin,” Universidade Estadual de Campinas, 13083-859 Campinas, São Paulo, Brazil*²*Department of Physics, University of Maryland, Baltimore County, Baltimore, Maryland 21250, USA*

(Received 16 October 2021; accepted 6 January 2022; published 24 January 2022)

Linear irreversible thermodynamics predicts that the entropy production rate can become negative. We demonstrate this prediction for metals under AC driving whose conductivity is well described by the Drude-Sommerfeld model. We then show that these negative rates are fully compatible with stochastic thermodynamics, namely, that the entropy production does fulfill a fluctuation theorem. The analysis is concluded with the observation that the stochastic entropy production as defined by the surprisal or ignorance of the Shannon information does not agree with the phenomenological approach.

DOI: [10.1103/PhysRevE.105.L012105](https://doi.org/10.1103/PhysRevE.105.L012105)

Introduction. The only processes that are fully describable by means of traditional thermodynamics are infinitely slow successions of equilibrium states [1]. Whereas considering such idealized situations is well suited to formulate universal statements, its practical insight is somewhat limited. All real processes occur at finite rates, and, therefore, entropy is irretrievably lost into the environment. Historically the first attempt to quantify this entropy “production” was developed in *linear irreversible thermodynamics* [2,3]. The central assumption of this generalized theory is that fluxes depend only linearly on the forces driving the system away from equilibrium. Its results are obtained from a combination of the local equilibrium hypothesis with conservation laws. The textbook example is heat conduction generated by a temperature gradient, which is described by Fourier’s law [4].

An even more widely known example of such linear problems is electrical conduction, that is described by Ohm’s law. Nevertheless, there are still subtleties to be unveiled. Only recently, we showed in Ref. [5] that the entropy production in noble metals under AC driving exhibits nonmonotonic growth as a function of time. In other words, in electrical conduction the entropy production rate can become negative. Such negative rates occur in situations in which the external driving is too fast for the system to react, and, hence, the response lacks behind the overall dynamics. Similar observations have been reported in, e.g., viscoelastic fluids [6] and single-level quantum dots [7] under oscillatory driving and in freely expanding ideal gases [8]. Interestingly, negative entropy production rates in open systems undergoing non-Markovian dynamics are somewhat commonplace [9–13]. However, our analysis is entirely based on the lag of response [14,15], which also gives rise to negative rates in Markovian settings [5,16].

Even more remarkably, negative entropy production rates are not indicative of scenarios operating far from thermal equilibrium, but they can be observed fully within the regime of

linear irreversible thermodynamics [16]. Since this approach fully rests on phenomenological and macroscopic arguments, the considered entropy production is often considered as genuinely thermodynamic.

A more modern approach to nonequilibrium problems is *stochastic thermodynamics* [17]. Arguably, the most central notion is the stochastic entropy production, which is defined as a statistical or rather information theoretic quantity. Whereas in linear irreversible thermodynamics the entropy production is expressed as a bilinear form of fluxes and forces, in stochastic thermodynamics, we have the “surprisal,” i.e., the logarithm of the system’s distribution in state space [18]. The main results of stochastic thermodynamics are the fluctuation theorems, which quantify that negative fluctuations of the entropy production are exponentially suppressed [18–20].

The natural question arises, whether the two paradigms are consistent with each other, or rather whether the two “versions” of entropy production are equivalent. In particular, the occurrence of negative rates in irreversible thermodynamics [5,6,16] appears incompatible with the strict positivity of the stochastic entropy production rate often discussed in the literature [21–34].

In the present Letter, we show that the entropy production as defined in linear irreversible thermodynamics indeed fulfills a fluctuation theorem. For pedagogical reasons and for specificity we focus on electrical conduction in Drude-Sommerfeld metals [35–38] under AC driving. Despite its somewhat crude approximations, experiments have shown that the Drude model, combined with Fermi-Dirac statistics, does describe properties of real metals, such as gold, copper, and silver [39,40] at room temperature and low photon energies. However, the validity of our results is not restricted to electric conduction. Rather, it is easy to see that our analysis remains valid for other situations that can be described with the linear framework. Finally, we will also see that the irreversible entropy production and the stochastic entropy production are typically different, and that they only become identical in the limit of infinitely slow driving.

*mbonanca@ifi.unicamp.br

†deffner@umbc.edu

Irreversible thermodynamics. To keep the discussion self-contained, we begin by briefly reviewing the approach, and by establishing notions and notations. In our analysis, we use irreversible thermodynamics to derive an expression for the entropy production (EP) rate for a situation in which monochromatic and polarized light is shined on a piece of metal. In this case, the balance equation for the electromagnetic energy density $u_{\text{EM}}(\mathbf{r}, t)$ reads

$$\frac{\partial u_{\text{EM}}}{\partial t} + \nabla \cdot \mathbf{S} = -\mathbf{J}_e \cdot \mathbf{E}, \quad (1)$$

where \mathbf{S} is the Poynting vector. Equation (1) contains a source term which describes the power density lost to the charge carriers, which is the product of the electrical current density \mathbf{J}_e and the electric field \mathbf{E} .

Accordingly, the balance equation for the internal energy density $u(\mathbf{r}, t)$ of the charge carriers becomes,

$$\frac{\partial u}{\partial t} + \nabla \cdot \mathbf{J}_u = \mathbf{J}_e \cdot \mathbf{E}, \quad (2)$$

where \mathbf{J}_u denotes the flux of internal energy and due to energy conservation the source term has the opposite sign. Further assuming a constant number of charge carriers, we also have the balance equation for the entropy density $s(\mathbf{r}, t)$,

$$\frac{\partial s}{\partial t} + \nabla \cdot \mathbf{J}_s = \dot{\bar{\Sigma}}, \quad (3)$$

whose source term is the EP rate we want to obtain.

Combining Eqs. (2) and (3) with the local equilibrium hypothesis [see Eq. (A3) and Appendix A], we obtain

$$\dot{\bar{\Sigma}} = \mathbf{J}_u \cdot \nabla \left(\frac{1}{T} \right) - \mathbf{J}_n \cdot \nabla \left(\frac{\mu}{T} \right) + \frac{\mathbf{J}_e \cdot \mathbf{E}}{T}, \quad (4)$$

whose last term is the contribution from electrical conduction. The quantities T and μ denote, respectively, the temperature and the chemical potential imposed on the set of charge carriers as scalar fields, and \mathbf{J}_n is the particle flux.

Temperature, chemical potential, and pressure gradients are constrained by the Gibbs-Duhem equation [41] (see Appendix A), which implies that under uniform temperature and pressure, the EP rate simply becomes

$$\dot{\bar{\Sigma}} = \frac{\mathbf{J}_e \cdot \mathbf{E}}{T}. \quad (5)$$

Additionally, phenomenological linear relations between currents and forces are assumed to hold. In electrical conduction, such a relation exists in the frequency domain [42],

$$\hat{J}_{e,i}(\omega) = \sum_j \sigma_{ij}(\omega) \hat{E}_j(\omega), \quad (6)$$

i.e., between the Fourier transforms of the electrical current $\hat{J}_{e,i}(\omega)$ and the electric field $\hat{E}_j(\omega)$ along the i and j directions, respectively. Note that Eq. (6) is nothing but Ohm's law with the conductivity tensor $\sigma_{ij}(\omega)$.

To evaluate the EP rate $\dot{\bar{\Sigma}}$ (5), an expression for the current in time domain is required. The inverse Fourier transform of Eq. (6) reads

$$J_{e,i}(t) = \int_{-\infty}^t dt' \sum_j \Phi_{ij}(t-t') E_j(t'), \quad (7)$$

where $\Phi_{ij}(t)$ denotes the response function [42]. Equation (7) describes possible memory effects since current and electric field are not evaluated at the same instant in time [14,42]. Combining Eq. (7) and the bilinear form (5) for $\dot{\bar{\Sigma}}$, we obtain

$$\dot{\bar{\Sigma}} = \frac{1}{T} \sum_{i,j} E_i(t) \int_{-\infty}^t dt' \Phi_{ij}(t-t') E_j(t'). \quad (8)$$

This expression contrasts the more common case in which thermodynamic forces are evaluated at the same instant in time, and the EP rate remains strictly positive, see, for instance, Refs. [24,29,30].

Drude-Sommerfeld entropy production. In the Drude model, the charge carriers in an ideal metal are described as a classical free electron gas which obeys Maxwell-Boltzmann statistics [35,36]. In its extension to the quantum domain, the equilibrium statistics is upgraded to the Fermi-Dirac one, and the quantum effects are encoded in the density N of charge carriers at the Fermi level, in the behavior of the relaxation time with temperature, and in the effective (band) mass m of the electrons [37,38,43].

Whereas an ideal gas is strictly free of collisions, assuming a finite relaxation time in the Drude model implies a finite mean free path. This mean free path is justified by considering the scattering of the charge carriers with phonons and impurities [38]. It can be phenomenologically introduced expressing the collision term of the Boltzmann equation as [43], $(\partial \rho / \partial t)_{\text{coll}} = -\delta \rho / \tau_R$, where τ_R , ρ , and $\delta \rho = \rho - \rho_0$ denote the relaxation time, the nonequilibrium distribution, and the deviation from the initial equilibrium distribution ρ_0 , respectively.

Hence, we obtain for the conductivity,

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega \tau_R}, \quad (9)$$

where $\sigma_0 = Nq^2\tau_R/m$ is the DC conductivity in the zero-frequency limit [43] and q denotes the electric charge.

Computing the inverse Fourier transform of Eq. (9), we obtain the response function,

$$\Phi(t) = \Theta(t) \frac{\sigma_0}{\tau_R} \exp(-|t|/\tau_R), \quad (10)$$

and $\Theta(t)$ is the Heaviside step function. Hence, the EP rate (8) becomes

$$\dot{\bar{\Sigma}} = \frac{\sigma_0}{T \tau_R} E(t) \int_0^t dt' \exp(-|t-t'|/\tau_R) E(t'). \quad (11)$$

Assuming a monochromatic electric field, $E(t) = E_0 \sin(\omega_0 t)$, and employing Eq. (11), the entropy production rate (8) reads

$$\dot{\bar{\Sigma}} = \frac{1}{T} \frac{\sigma_0 E_0^2 \sin(\omega_0 t)}{1 + (\omega_0 \tau_R)^2} [\omega_0 \tau_R \exp(-t/\tau_R) - \omega_0 \tau_R \cos(\omega_0 t) + \sin(\omega_0 t)]. \quad (12)$$

Figure 1 illustrates Eq. (12) for different values of $\omega_0 \tau_R$. As discussed in Ref. [5], negative values of $\dot{\bar{\Sigma}}$ persist within a small vicinity of $\omega_0 t = n\pi$, $n = 1, 2, 3, \dots$, as $\omega_0 \tau_R$ decreases and vanishes only in the limit $\omega_0 \tau_R \rightarrow 0$.

The emergence of negative values of $\dot{\bar{\Sigma}}$ can be understood qualitatively from Eq. (11). $\dot{\bar{\Sigma}}$ is given by the product of a

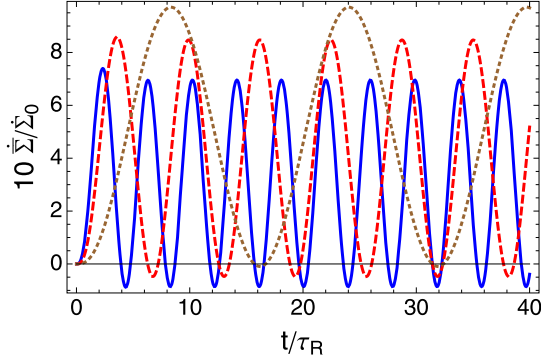


FIG. 1. Entropy production rate (12) as a function of t/τ_R for different values of $\omega_0\tau_R$. Solid-blue, dashed-red, and dotted-brown lines correspond to $\omega_0\tau_R = 0.8, 0.5$, and 0.2 , respectively. Units are $\dot{\Sigma}_0 \equiv \sigma_0 E_0^2/T$.

time-dependent electric field and a convolution between the same field (evaluated at a previous time) and the response function. This describes a delay between the response of the system and the electric field. Thus, if the function $E(t)$ is nonmonotonic and acquires negative values, negative values of $\dot{\Sigma}$ occur [44].

Fluctuation theorem. As mentioned before, Drude originally considered the charge carriers as a classical gas of particles following Maxwell-Boltzmann statistics. Although this leads to wrong predictions of the DC conductivity σ_0 , it does not change the form of $\sigma(\omega)$ given by Eq. (9). This means that the qualitative features of the EP rate $\dot{\Sigma}$ and its expression (12) remain unaltered in the original Drude model, although with a different value of σ_0 .

For the next part of the analysis, we restrict ourselves to the classical Drude model and develop the corresponding stochastic thermodynamics. Here, N denotes the *number* (instead of density) of noninteracting charge carriers, and by J_e , we denote the electrical current (instead of current density). We start by combining Ohm's law (6) with the Drude conductivity (9),

$$\hat{J}_e(\omega) = \frac{\sigma_0}{1 - i\omega\tau_R} \hat{E}(\omega), \quad (13)$$

which in the time domain takes the form of the following equation of motion for $J_e(t)$:

$$\frac{dJ_e}{dt} + \frac{J_e}{\tau_R} = \frac{\sigma_0}{\tau_R} E(t). \quad (14)$$

Recalling that $J_e(t)$ is defined as $J_e(t) = Nq\langle p(t) \rangle/m$, where $\langle p(t) \rangle$ is the average momentum of a charge carrier along the direction of the electric field, Eq. (14) yields

$$\frac{d\langle p(t) \rangle}{dt} + \frac{\langle p(t) \rangle}{\tau_R} = qE(t), \quad (15)$$

and $\sigma_0 = Nq^2\tau_R/m$.

Fluctuations can be introduced by removing the average in Eq. (15) and introducing a Gaussian-distributed white-noise $f_i(t)$ with zero mean acting on the i th charged particle. The equation of motion for the fluctuating linear momentum of

the i th charge along the direction of $E(t)$ then reads

$$\frac{dp_i(t)}{dt} + \frac{p_i(t)}{\tau_R} = qE(t) + f_i(t), \quad (16)$$

which is nothing but Brownian motion under the external force $qE(t)$. The fluctuating current $j_e(t)$ then is as follows:

$$j_e(t) = \frac{q}{m} \sum_{i=1}^N p_i(t), \quad (17)$$

and we define the fluctuating entropy production,

$$\Sigma(t) = \frac{1}{T} \int_0^t dt' j_e(t') E(t'), \quad (18)$$

inspired by irreversible thermodynamics [see Eq. (5)].

Since the $p_i(t)$ are Gaussian distributed and $\Sigma(t)$ is a linear transformation of their sum, the probability distribution of $\Sigma(t)$ will be Gaussian as well. See Refs. [45,46] for similar arguments. From the solution of Eq. (16) and expression (18), it can be shown that (see Appendix B)

$$\langle \Sigma(t) \rangle = \frac{Nq^2}{mT} \int_0^t dt' \int_0^{t'} dt'' E(t') \exp[-(t' - t'')/\tau_R] E(t''). \quad (19)$$

when the linear momenta of the charge carriers are distributed according to Maxwell's distribution at $t = 0$.

Under the same assumptions, we have (see Appendix B)

$$\begin{aligned} \langle \Sigma^2(t) \rangle &= \langle \Sigma(t) \rangle^2 + k_B \frac{Nq^2}{mT} \int_0^t dt' \int_0^t dt'' E(t') \\ &\quad \times \exp(-|t' - t''|/\tau_R) E(t''), \end{aligned} \quad (20)$$

and we obtain

$$\text{Var}[\Sigma(t)] = \langle \Sigma^2(t) \rangle - \langle \Sigma(t) \rangle^2 = 2k_B \langle \Sigma(t) \rangle. \quad (21)$$

The probability distribution of Σ then reads

$$P(\Sigma) = \frac{1}{\sqrt{2\pi \text{Var}[\Sigma]}} \exp\left(-\frac{[\Sigma - \langle \Sigma \rangle]^2}{2\text{Var}[\Sigma]}\right), \quad (22)$$

which implies the detailed fluctuation theorem,

$$\frac{P(\Sigma)}{P(-\Sigma)} = \exp\left[\frac{2\langle \Sigma \rangle \Sigma}{\text{Var}(\Sigma)}\right] = \exp\left(\frac{\Sigma}{k_B}\right). \quad (23)$$

and its integral version, $\langle \exp(-\Sigma/k_B) \rangle = 1$.

Note that the average EP rate is as follows:

$$\langle \dot{\Sigma}(t) \rangle = \frac{Nq}{mT} \langle p(t) \rangle E(t), \quad (24)$$

whose time integral is identical to Eq. (19) and with different values and units of σ_0 in Eq. (11). Hence, we conclude that negative values of the EP rate are not incompatible with the fluctuation theorem (23) and, hence, the second law.

Entropy production from microreversibility. As a next step, we show that the expression (18) for the EP appears naturally from microreversibility [19], i.e., from the comparison of probabilities of observing a given trajectory and its time-reversed conjugated twin [47–50].

Considering Eq. (16) for a single charge carrier, its corresponding Fokker-Planck equation reads [51] (we have

dropped the index i)

$$\frac{\partial}{\partial t} \mathcal{W}(p, t) = -\frac{\partial}{\partial p} \left[\left(-\frac{p}{\tau_R} + qE(t) \right) \mathcal{W}(p, t) \right] + \frac{\partial^2}{\partial p^2} \left(\frac{mk_B T}{\tau_R} \mathcal{W}(p, t) \right), \quad (25)$$

where $\mathcal{W}(p, t)$ denotes the probability density of linear momentum at a given t . Following the standard procedures [51], it is straightforward to obtain the path-integral solution of Eq. (25) [47,48,51].

In this formulation, the time evolution of $\mathcal{W}(p, t)$ is expressed in terms of probabilities of trajectories. Denoting by $\mathcal{P}[\Gamma|p_0]$ the conditional probability of observing a trajectory Γ that starts at p_0 , its expression reads

$$\mathcal{P}[\Gamma|p_0] = \mathcal{N} \exp \left\{ -\int_0^t dt' \mathcal{L}[p(t'), \dot{p}(t'); E(t')] \right\}, \quad (26)$$

where

$$\mathcal{L}[p(t'), \dot{p}(t'); E(t')] = \frac{[\dot{p}(t') - [-p(t')/\tau_R + qE(t')]]^2}{4mk_B T/\tau_R}, \quad (27)$$

and \mathcal{N} is a normalization factor [51].

Following Ref. [47], we define Γ^\dagger as the time-reversed conjugated twin of Γ for the time-reversed electric field $E^R(t)$. Thus, the probability of observing Γ^\dagger is given by

$$\mathcal{P}[\Gamma^\dagger | -p_t] = \mathcal{N} \exp \left\{ -\int_0^t dt' \mathcal{L}[p^\dagger(t'), \dot{p}^\dagger(t'); E^R(t')] \right\}, \quad (28)$$

where the initial condition $-p_t$ of Γ^\dagger is the time-reversal of the final point of Γ .

Combining Eqs. (26) and (28) we have the microreversibility condition (see Appendix C),

$$\frac{\mathcal{P}[\Gamma|p_0]}{\mathcal{P}[\Gamma^\dagger | -p_t]} = \exp \left\{ -\frac{(p_t^2 - p_0^2)}{2mk_B T} + \frac{q}{mk_B T} \int_0^t dt' p(t') E(t') \right\}, \quad (29)$$

where the second term in the exponent is proportional to the single-particle version of Eq. (18). This term can be understood as proportional to the fluctuating power input due to the electric field. On the other hand, the first term in the exponent is proportional to the variation of the stochastic internal energy (which in the present case is purely kinetic) between the final and the initial states. Hence, energy conservation implies that the entire exponent is equal to the heat absorbed by the heat bath in units of $k_B T$ [19,47,48,50].

Entropy production from Shannon information. In the preceding sections, we showed how the fluctuating entropy production can be found in full consistency with linear irreversible thermodynamics. In stochastic thermodynamics, however, the EP is often obtained from the Shannon information [17],

$$S(t) = -k_B \int dp \mathcal{W}(p, t) \ln \mathcal{W}(p, t), \quad (30)$$

for the solution $\mathcal{W}(p, t)$ of Eq. (25) [18]. Following standard arguments [17,28], we have

$$\frac{1}{k_B} \frac{dS}{dt} = \frac{\tau_R}{mk_B T} \int dp \frac{\mathcal{J}(p, t)^2}{\mathcal{W}(p, t)} + \frac{1}{mk_B T} \int dp p \mathcal{J}(p, t) = \Pi(t) - \Omega(t), \quad (31)$$

where

$$\mathcal{J}(p, t) = -\frac{p}{\tau_R} \mathcal{W}(p, t) - \frac{\partial}{\partial p} \left(\frac{mk_B T}{\tau_R} \mathcal{W}(p, t) \right). \quad (32)$$

The term denoted by $\Omega(t)$,

$$\Omega(t) = -\frac{1}{mk_B T} \int dp p \mathcal{J}(p, t) \quad (33)$$

is typically called the entropy flux [17] and the non-negative term,

$$\Pi(t) = \frac{\tau_R}{mk_B T} \int dp \mathcal{W}(p, t) \left(\frac{\mathcal{J}(p, t)}{\mathcal{W}(p, t)} \right)^2 \quad (34)$$

is taken as the EP rate [17,27,28].

The terminology and interpretation of the terms in Eq. (31) make contact with the balance equation (3) introduced in the macroscopic approach of irreversible thermodynamics. However, the fact that $\Pi(t)$ is always non-negative already shows a strong disagreement with the EP rates discussed in the previous sections. Additionally, it is easy to see that $\Pi(t)$ does not have the bilinear form discussed in Sec. II.

Consider the solution of Eq. (25) [46,52],

$$\mathcal{W}(p, t) = (2\pi mk_B T)^{-1/2} \exp \left(-\frac{[p - \langle p(t) \rangle]^2}{2mk_B T} \right) \quad (35)$$

for an initial Maxwell-Boltzmann distribution. Then, the average momentum $\langle p(t) \rangle$ is as follows:

$$\langle p(t) \rangle = \int_0^t dt' \exp[-(t-t')/\tau_R] qE(t'), \quad (36)$$

which is obtained from Eq. (15). Plugging expression (35) in Eq. (34), it is straightforward to show that,

$$k_B \Pi(t) = \frac{\langle p(t) \rangle^2}{mT \tau_R}, \quad (37)$$

which is clearly different from current $q\langle p(t) \rangle/m$ times thermodynamic force $E(t)/T$, which we had before in Eq. (24). However, note that Eqs. (24) and (37) do become identical in the limit of infinitely slow driving, i.e., $\omega_0 \tau_R \rightarrow 0$. Equation (13) tells us that the delay between $J_e(t)$ and $E(t)$ vanishes in this limit, i.e., the current becomes simply proportional to the electric field.

Additionally, the solution (35) leads to the following expression for the entropy flux $\Omega(t)$:

$$k_B \Omega(t) = \frac{\langle p(t) \rangle^2}{mT \tau_R}. \quad (38)$$

Together with Eq. (37), this implies that the time derivative of the Shannon information (30) is zero whether the system is in the transient or long-time state.

Concluding remarks. Motivated by the macroscopic approach of irreversible thermodynamics, we have defined an expression for the fluctuating EP in the classical Drude model.

We have shown that this quantity fulfills a fluctuation theorem despite the existence of negative values of its corresponding rate. Hence, this shows, for a paradigmatic example, that negative entropy production rates are not incompatible with the fluctuation theorem and the second law. Moreover, we have shown that the entropy production rate obtained from the Shannon entropy and the Fokker-Planck equation contrasts with our expression and does not have the bilinear form predicted by irreversible thermodynamics. In addition, we have shown that the Shannon information remains constant along the transition from the initial equilibrium state to long-time nonequilibrium one and that the entropy production obtained from it is simply proportional to the power related to the friction force. Our expression, however, is a measure of the total amount of energy absorbed by the insulated system composed of the set of charge carriers and its heat bath.

Acknowledgments. We acknowledge comments by J. Thingna and K. Ptaszyński. M.V.S.B. acknowledges financial support from FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) (Brazil) (Grant No. 2020/02170-4).

APPENDIX A: IRREVERSIBLE THERMODYNAMICS

In this Appendix, we give a short derivation of Eq. (5) for the EP rate in irreversible thermodynamics. The hypothesis of local equilibrium allows to extend standard relations of equilibrium thermodynamics to the nonequilibrium regime [41]. For instance, the combination of the first with the second law,

$$T ds = du - \mu dn, \quad (\text{A1})$$

and the Gibbs-Duhem equation,

$$s dT = -dP - n d\mu \quad (\text{A2})$$

are assumed to hold when the temperature T , the pressure P , and the chemical potential μ along with the densities of entropy s , internal energy u , and particles n , are treated as scalar fields.

Using Eqs. (A1) and (A2), it is possible to write [41]

$$\frac{du}{dt} - T \frac{ds}{dt} - \mu \frac{dn}{dt} = \frac{\partial u}{\partial t} - T \frac{\partial s}{\partial t} - \mu \frac{\partial n}{\partial t} = 0, \quad (\text{A3})$$

through which the balance equations can be connected. Considering Eqs. (2), (3), and conservation of particles,

$$\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{J}_n = 0, \quad (\text{A4})$$

it is possible to find for the entropy flux,

$$\mathbf{J}_s = \frac{\mathbf{J}_u}{T} - \mu \frac{\mathbf{J}_n}{T}, \quad (\text{A5})$$

and the EP rate,

$$\dot{\Sigma} = \mathbf{J}_u \cdot \nabla \left(\frac{1}{T} \right) - \mathbf{J}_n \cdot \nabla \left(\frac{\mu}{T} \right) + \frac{\mathbf{J}_e \cdot \mathbf{E}}{T}. \quad (\text{A6})$$

Under the conditions of uniform temperature and pressure, the Gibbs-Duhem equation in the form

$$\nabla P + s \nabla T + n \nabla \mu = 0 \quad (\text{A7})$$

implies that $\nabla \mu = 0$ and Eq. (A5) reduces to

$$\dot{\Sigma} = \frac{\mathbf{J}_e \cdot \mathbf{E}}{T}. \quad (\text{A8})$$

APPENDIX B: THE FIRST TWO MOMENTS OF $\Sigma(t)$

To calculate the first moment $\langle \Sigma(t) \rangle$, we start with Eq. (18) and the solution $p(t)$ of Eq. (16),

$$p_i(t) = p_i(0)e^{-t/\tau_R} + \int_0^t dt' \exp[-(t-t')/\tau_R] qE(t') + \int_0^t dt' \exp[-(t-t')/\tau_R] f_i(t'). \quad (\text{B1})$$

Assuming that the system is in equilibrium at $t = 0$, we insert the previous expression in Eq. (18) and, after taking the average, Eq. (19) is obtained using $\langle p_i(0) \rangle = 0$ and $\langle f_i(t) \rangle = 0$.

To obtain the second moment $\langle \Sigma^2(t) \rangle$, we take the average of Eq. (18) squared, which reads

$$\langle \Sigma^2(t) \rangle = \left(\frac{q}{mT} \right)^2 \int_0^t ds \int_0^t du E(s)E(u) \sum_{i,j} \langle p_i(s)p_j(u) \rangle. \quad (\text{B2})$$

Using again the solution (B1), the initial condition $\langle p_i(0)p_j(0) \rangle = \delta_{ij}mk_B T$ and the white-noise property,

$$\langle f_i(t)f_j(t') \rangle = \frac{2mk_B T}{\tau_R} \delta_{ij} \delta(t-t'), \quad (\text{B3})$$

where δ_{ij} is Kronecker's δ and $\delta(t)$ is Dirac's δ function, it is possible to show that

$$\langle p_i(s)p_j(u) \rangle = \delta_{ij}mk_B T e^{-|s-u|/\tau_R} + q^2 \int_0^s dt' \int_0^u dt'' \exp[-(s+u-t'-t'')/\tau_R] E(t')E(t''). \quad (\text{B4})$$

Plugging the previous expression into Eq. (B2), we finally obtain

$$\begin{aligned} \langle \Sigma^2(t) \rangle &= \langle \Sigma(t) \rangle^2 \\ &+ k_B \frac{Nq^2}{mT} \int_0^t ds \int_0^t du \exp(-|s-u|/\tau_R) E(s)E(u) \\ &= \langle \Sigma(t) \rangle^2 + 2k_B \langle \Sigma(t) \rangle. \end{aligned} \quad (\text{B5})$$

APPENDIX C: CONDITIONAL PROBABILITY OF TIME-REVERSED TRAJECTORIES

In this Appendix, we explain what is meant by the “action” appearing in Eq. (28). First, we clarify that $p^\dagger(t') = -p(t-t')$, $\dot{p}^\dagger(t') = \dot{p}(t-t')$, and $E^R(t') = E(t-t')$, where $p(t)$ refers to the trajectory Γ whose evolution is subjected to $E(t)$. Using then Eq. (27), we obtain

$$\begin{aligned} \mathcal{L}[p^\dagger(t'), \dot{p}^\dagger(t'); E^R(t')] &= \frac{\{\dot{p}(t-t') - [p(t-t')/\tau_R + qE(t-t')]\}^2}{(4mk_B T/\tau_R)}. \end{aligned} \quad (\text{C1})$$

which implies that,

$$\begin{aligned} & \int_0^t dt' \mathcal{L}[p^\dagger(t'), \dot{p}^\dagger(t'); E^R(t')] \\ &= \int_0^t ds' \frac{\{\dot{p}(s') - [p(s')/\tau_R + qE(s')]\}^2}{(4mk_B T/\tau_R)}, \quad (\text{C2}) \end{aligned}$$

after the change in variables $s' = t - t'$. Finally, the conditional probability of observing the trajectory Γ^\dagger under the time-reversed field $E^R(t)$ reads

$$\mathcal{P}[\Gamma^\dagger | -p_t] = \mathcal{N} \exp \left\{ - \int_0^t ds' \frac{\{\dot{p}(s') - [p(s')/\tau_R + qE(s')]\}^2}{(4mk_B T/\tau_R)} \right\}, \quad (\text{C3})$$

-
- [1] H. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, New York, USA, 1985).
- [2] I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes* (Interscience, New York, 1961).
- [3] S. R. De Groot and P. Mazur, *Nonequilibrium Thermodynamics* (Dover, New York, 1984).
- [4] R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, Oxford, UK, 2001).
- [5] M. V. S. Bonança, P. Nazé, and S. Deffner, Negative entropy production rates in drude-sommerfeld metals, *Phys. Rev. E* **103**, 012109 (2021).
- [6] S. R. Williams, D. J. Evans, and E. Mittag, Negative entropy production in oscillatory processes, *C. R. Phys.* **8**, 620–624 (2007).
- [7] J. Thingna, F. Barra, and M. Esposito, Kinetics and thermodynamics of a driven open quantum systems, *Phys. Rev. E* **96**, 052132 (2017).
- [8] S. Chakraborti, A. Dhar, S. Goldstein, A. Kundu, and J. L. Lebowitz, Entropy growth during free expansion of an ideal gas, *arXiv:2109.07742*.
- [9] S. Bhattacharya, A. Misra, C. Mukhopadhyay, and A. K. Pati, Exact master equation for a spin interacting with a spin bath: Non-markovianity and negative entropy production rate, *Phys. Rev. A* **95**, 012122 (2017).
- [10] S. Marcantoni, S. Alipour, F. Benatti, R. Floreanini, and A. T. Rezakhani, Entropy production and non-markovian dynamical maps, *Sci. Rep.* **7**, 12447 (2017).
- [11] Y. Y. Xu, J. Liu, and M. Feng, Positive entropy production rate induced by non-markovianity, *Phys. Rev. E* **98**, 032102 (2018).
- [12] M. Popovic, B. Vacchini, and S. Campbell, Entropy production and correlations in a controlled non-markovian setting, *Phys. Rev. A* **98**, 012130 (2018).
- [13] P. Strasberg and M. Esposito, Non-markovianity and negative entropy production rates, *Phys. Rev. E* **99**, 012120 (2019).
- [14] R. Zwanzig, Memory effects in irreversible thermodynamics, *Phys. Rev.* **124**, 983 (1961).
- [15] J. A. McLennan, Entropy production for a medium with memory, *J. Chem. Phys.* **41**, 1159 (1964).
- [16] P. Nazé and M. V. S. Bonança, Compatibility of linear-response theory with the second law of thermodynamics and the emergence of negative entropy production rates, *J. Stat. Mech.* (2020) 013206.
- [17] L. Peliti and S. Pigolotti, *Stochastic Thermodynamics* (Princeton University Press, New Jersey, 2021).
- [18] U. Seifert, Entropy Production Along a Stochastic Trajectory and an Integral Fluctuation Theorem, *Phys. Rev. Lett.* **95**, 040602 (2005).
- [19] G. E. Crooks, Entropy production fluctuation theorem and nonequilibrium work relation for free energy differences, *Phys. Rev. E* **60**, 2721 (1999).
- [20] M. Esposito and C. Van den Broeck, Three Detailed Fluctuation Theorems, *Phys. Rev. Lett.* **104**, 090601 (2010).
- [21] H. Spohn, Entropy production for quantum dynamical semi-groups, *J. Math. Phys.* **19**, 1227 (1978).
- [22] I. Prigogine and J. G  h  n  au, Entropy, matter, and cosmology, *Proc. Natl. Acad. Sci. USA* **83**, 6245 (1986).
- [23] D. Ruelle, Positivity of entropy production in nonequilibrium statistical mechanics, *J. Stat. Phys.* **85**, 1 (1996).
- [24] C. Maes, F. Redig, and A. Van Moffaert, On the definition of entropy production, via examples, *J. Math. Phys.* **41**, 1528 (2000).
- [25] J. I. Beldria, Positive and negative entropy production in an ideal-gas expansion, *Europhys. Lett.* **70**, 446 (2005).
- [26] M. Esposito and C. Van den Broeck, Three faces of the second law. i. master equation formulation, *Phys. Rev. E* **82**, 011143 (2010).
- [27] C. Van den Broeck and M. Esposito, Three faces of the second law. ii. fokker-planck formulation, *Phys. Rev. E* **82**, 011144 (2010).
- [28] T. Tom   and M. J. de Oliveira, Entropy production in irreversible systems described by a fokker-planck equation, *Phys. Rev. E* **82**, 021120 (2010).
- [29] M. Bauer, K. Brandner, and U. Seifert, Optimal performance of periodically driven, stochastic heat engines under limited control, *Phys. Rev. E* **93**, 042112 (2016).
- [30] K. Brandner and U. Seifert, Periodic thermodynamics of open quantum systems, *Phys. Rev. E* **93**, 062134 (2016).
- [31] S. Deffner, Kibble-zurek scaling of the irreversible entropy production, *Phys. Rev. E* **96**, 052125 (2017).
- [32] H. Jabraoui, S. Ouaskit, J. Richard, and J.-L. Garden, Determination of the entropy production during glass transition: theory and experiment, *J. Non-Cryst. Sol.* **533**, 119907 (2020).
- [33] G. T. Landi and M. Paternostro, Irreversible entropy production, from quantum to classical, *Rev. Mod. Phys.* **93**, 035008 (2021).
- [34] S. Deffner and M. V. S. Bonança, Thermodynamic control—An old paradigm with new applications, *Europhys. Lett.* **131**, 20001 (2020).
- [35] P. Drude, Zur Elektronentheorie der Metalle, *Ann. Phys. (NY)* **306**, 566 (1900).
- [36] P. Drude, Zur Elektronentheorie der Metalle; II. Teil. Galvanomagnetische und thermomagnetische Effecte, *Ann. Phys. (NY)* **308**, 369 (1900).

- [37] A. Sommerfeld, Zur Elektronentheorie der Metalle auf Grund der Fermischen Statistik, *Z. Phys.* **47**, 1 (1928).
- [38] J. Bardeen, Electrical conductivity of metals, *J. Appl. Phys.* **11**, 88 (1940).
- [39] R. L. Olmon, B. Slovick, T. W. Johnson, D. Shelton, S.-H. Oh, G. D. Boreman, and M. B. Raschke, Optical dielectric function of gold, *Phys. Rev. B* **86**, 235147 (2012).
- [40] H. U. Yang, J. D'Archangel, M. L. Sundheimer, E. Tucker, G. D. Boreman, and M. B. Raschke, Optical dielectric function of silver, *Phys. Rev. B* **91**, 235137 (2015).
- [41] L. E. Reichl, *A Modern Course in Statistical Physics* (Wiley-VCH, Weinheim, 2016).
- [42] R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II: Nonequilibrium Statistical Mechanics*, Springer Series in Solid-State Sciences Vol. 31 (Springer-Verlag, Heidelberg, 1991).
- [43] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College Publishing, Philadelphia, 1976).
- [44] Note, however, that it has been shown that the entropy production, $\overline{\Sigma} = \int_0^t dt' \dot{\sigma} F \overline{\Sigma}$, itself remains positive at all times [5,16].
- [45] R. van Zon and E. G. D. Cohen, Stationary and transient work-fluctuation theorems for a dragged brownian particle, *Phys. Rev. E* **67**, 046102 (2003).
- [46] J. I. Jiménez-Aquino, Entropy production theorem for a charged particle in an electromagnetic field, *Phys. Rev. E* **82**, 051118 (2010).
- [47] V. Y. Chernyak, M. Chertkov, and C. Jarzynski, Path-integral analysis of fluctuation theorems for general langevin processes, *J. Stat. Mech.* (2006), P08001.
- [48] A. Imparato and L. Peliti, Fluctuation relations for a driven brownian particle, *Phys. Rev. E* **74**, 026106 (2006).
- [49] S. Deffner, M. Brunner, and E. Lutz, Quantum fluctuation theorems in the strong damping limit, *Europhys. Lett.* **94**, 30001 (2011).
- [50] P. S. Pal and S. Deffner, Stochastic thermodynamics of relativistic brownian motion, *New J. Phys.* **22**, 073054 (2020).
- [51] H. Risken, *The Fokker-Planck Equation* (Springer-Verlag, Berlin, 1996).
- [52] L. Ferrari, Heavy (or large) ions in a fluid in an electric field: The fundamental solution of the fokker-planck equation and related questions, *J. Chem. Phys.* **118**, 11092 (2003).