

Quantum Theory of Entropy Production

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Submitted in partial fulfillment of the
requirements for the degree
of Doctor of Philosophy
in the Graduate School of Arts and Sciences

COLUMBIA UNIVERSITY

2018

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Abstract

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In this thesis we develop an approach to nonequilibrium quantum-statistical mechanics which is based on the consideration of the thermodynamic entropy as being a quantum observable with an associated hermitian operator and with its own equation of motion, from which the rate of entropy production can be studied. The relationship of this quantum observable—the expectation value of which is proved to obey the laws of thermodynamics and is thus called the thermodynamic entropy—with heat dissipation in quantum many-body systems is investigated in detail.

After showing how the classical theory of nonequilibrium thermodynamics is obtained from our entropy-production formalism in the limit of very weakly coupled subsystems of a larger isolated quantum system, the solution of the equation of motion for the thermodynamic entropy operator is formally obtained and applied to the case of electrons interacting with phonons and being driven by an external electric field, arriving at an explicit expression for the Joule heat without any *a priori* consideration of the rate of change of the energy of the system.

Finally, the formalism is applied to solve a puzzle introduced with the most basic model for atom-light interactions: the Jaynes-Cummings model. Without using the correct thermodynamic arguments implied by our entropy-production theory, this model leads to the conclusion that a stream of two-level atoms sent to a cavity filled with monochromatic photons—in the so called one-atom maser configuration—

thermalize, under off-resonant conditions, to a temperature different from that of the photons, casting doubts on the validity of the principle of conservation of energy.

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Acknowledgments

I am indebted to my adviser Andrew J. Millis for giving me the opportunity to work with him immediately after I arrived to Columbia and for being always there for discussions and mentorship during my years as a graduate student. I have learned a lot from his unique and intuitive approach to physical problems and it was because of his early suggestion to read Hershfield's paper on nonequilibrium quantum-statistical mechanics that I began the journey that brought me to the developments of this thesis. I also appreciate his support to attend scientific conferences.

I would like to express my gratitude to the professors in the defense committee: Igor Aleiner, David Reichman, Sebastian Will, and Robert Mawhinney, for their careful examination of my dissertation and valuable suggestions for improvement of the presentation. Thanks a lot also to professors Boris Altshuler and Igor Aleiner for giving positive feedback about the exclusion from this thesis of a quantum-mechanical theory, still under development, of Clausius' transformation theory of heat.

I am also grateful for so many fruitful discussions with Junichi Okamoto, Carlos J. Argüello, Eric Andrade, Se Young Park, Zhouan He, Runzhi Wang, Daniel Flanigan, Rainer Härtle, Guy Cohen, Louis-François Arsenault, Ara Go, Qiang Han, Dante Kennes and Andrew Wieteska; as well as the support of Professor Tomo Uemura to attend one of the workshops

organized during his course on the Frontiers of Condensed Matter Physics. I am also indebted to the Colombian Government—through its Administrative Department of Science and Technology—which in association with the Fulbright Commission helped to support my doctoral studies for five years.

Finally, I would like to dedicate my efforts to the memoir of my mother, the encouragement of my father, siblings, and the rest of my big family; the unconditional support and cares of my wife, Francy, who has accompanied me in the good and bad moments of all these years; and to my son, Samuel, who inspires me to work hard for a better future.

Chapter 1

Introduction

Thermodynamics has been the subject of study of a number of influential minds in the history of science, due to its direct connection with observable phenomena in daily life and because it does not require any model about the microscopic constituents of matter. Its explanation using statistical arguments about the dynamics of these constituents was initiated by Maxwell, Boltzmann and Clausius and unified by [Gibbs \(1902\)](#) at the end of the nineteenth century, with far reaching consequences and open questions which have remained until our days.

This thesis dedicates to the evaluation of the foundations and the incorporation of new concepts in the trajectory followed by the field of statistical mechanics as applied to nonequilibrium problems. It turns out that the original intend of this field to describe—from the statistics of the microscopic constituents of matter—the observations of thermodynamics, was somewhat obscured in nonequilibrium situations by taking as a dogma in quantum mechanics Gibb’s statistical interpretation [Gibbs \(1902\)](#) of the concept of entropy introduced by [Clausius \(1865\)](#).

This interpretation, incorporated by [von Neumann \(2010\)](#) into the quantum theory, works quite well under equilibrium conditions and indeed, as in the classical theory, provides a mechanism to develop the entire theory of equilibrium statistical mechanics by looking at those statistical ensembles which maximize the entropy [Jaynes \(1957a,b\)](#)

$$S_t = -\text{Tr}(\hat{\rho}_t \ln \hat{\rho}_t), \quad (1.1)$$

with given constraints set by the conservation laws, with the density matrix $\hat{\rho}_t$ being the quantum-mechanical analog of the classical probability density function satisfying Liouville equation, which in the quantum theory became best known as the von Neumann equation

$$i \frac{\partial \hat{\rho}_t}{\partial t} = [\hat{H}, \hat{\rho}_t] \equiv L \hat{\rho}_t, \quad (1.2)$$

with \hat{H} being the Hamiltonian of the system ($\hbar = 1$, $k_B = 1$).

It is immediately seen that we run into trouble if the above interpretation is naively extrapolated to nonequilibrium situations since, if the solution of (1.2)

$$\hat{\rho}_t = e^{-i\hat{H}t} \hat{\rho}_0 e^{i\hat{H}t}, \quad (1.3)$$

is substituted in (1.1), we arrive to the conclusion that

$$S_t = S_0, \quad (1.4)$$

for all times. This is readily seen by taking the trace in the basis diagonalizing $\hat{\rho}_t$ and realizing that the eigenvalues of $\hat{\rho}_t$ are the same as the eigenvalues of $\hat{\rho}_0$ since they are connected by the *unitary* transformation (1.3).

The problem with (1.4) is that, if a meaning is to be given to S_t as the *thermodynamic* entropy \mathcal{S}_t , then it must satisfy the requirement established by Clausius

$$\mathcal{S}_t \geq \mathcal{S}_0, \quad (1.5)$$

according to the process undergone by the system from time $t = 0$ to time t being reversible (equality) or irreversible (inequality), which is one of the statements of the second law of thermodynamics.

The solution of the problem encountered is then to be sought within one—or possibly both of—the following scenarios:

1. Having a density matrix $\hat{\rho}_t$ for an isolated system, the quantity (1.1) does not represent the thermodynamic entropy out of equilibrium, since it does not satisfy (1.5). A functional different from $-\text{Tr}(\cdot \ln \cdot)$ applied on the density matrix must be found, having the desired properties.
2. The quantum-statistical state described by $\hat{\rho}_t$ should evolve with an equation of motion different from (1.2), whose solution can explain “irreversible” thermodynamic behavior. However, since changing the equation of motion cannot be justified without assuming some contact between the system and an environment—ruled out if we adhere to the usual theoretical abstraction of an *isolated* system—thermodynamic behavior is then to be interpreted as the predictions resulting from a transformed density matrix $\mathcal{T}\hat{\rho}_t$ which does exhibit non-unitary evolution, where \mathcal{T} is a linear transformation acting on the operators representing observables of the systems.

As we shall discuss next, the mainstream research on entropy in nonequilibrium quantum statistical mechanics has followed the route established by scenario 2 for decades (and up to the present time) but *keeping*, in most cases, the functional $-\text{Tr}(\cdot \ln \cdot)$ applied on such transformed density matrices $\mathcal{T}\hat{\rho}_t$ as defining an entropy

$$S_{\mathcal{T}} = -\text{Tr}(\mathcal{T}\hat{\rho}_t \ln \mathcal{T}\hat{\rho}_t), \quad (1.6)$$

which can be shown to increase for nonequilibrium processes and correspond to the well-known equilibrium thermodynamic entropy for the equilibrium ensembles.

These previous approaches, briefly reviewed in section 1.2, implicitly or explicitly assume, in the spirit of Boltzmann, a *subjective* interpretation Jaynes (1957b) of the entropy as a measure of uncertainty of a probability distribution, since it is only in this way that a blinded acceptance of the functional $-\text{Tr}(\cdot \ln \cdot)$, applied on some transformed density matrix, can be justified as the *least* biased Shannon (1948) of all

such possible selections and yet be able to capture the properties of the equilibrium thermodynamic entropy via maximum-entropy statistical inference.

Our approach in this thesis, fully discussed and applied in chapters 2 and 3, considers the thermodynamic entropy as an *objective* reality which is thus subject to experimental measurement. As such, it should then be represented by a hermitian operator as all observables are in quantum mechanics, and its observations should be sharply distributed around its quantum-statistical average that we call the thermodynamic entropy.

Our selection of an expression for the thermodynamic entropy originates from our tenet of treating the entropy as a quantum observable, which thereby implies the consideration of both scenarios 1 and 2. That is, if the operation $\mathcal{T}\hat{\rho}_t$ on the density matrix $\hat{\rho}_t$ is to be performed in order to explain thermodynamic behavior, it would not be consistent to alter the Hilbert space of the system by \mathcal{T} , to represent the evolving thermodynamic state, without altering in the *same* way all other quantum observables which are chosen to represent thermodynamic quantities. This “uniformity” is very unique to thermodynamics, in which the *state* and the values of all the relevant *observables* represent the same entity.

The principle of uniformity then implies that if \hat{A} is a hermitian operator representing a quantum observable, *thermodynamic* measurements of this observable are better described by $\mathcal{T}\hat{A}$, provided \mathcal{T} is suitably chosen. In order to see how this determines our selection of an expression for the thermodynamic entropy we note that a starting point to identify it as a quantum observable is to define first a hermitian operator

$$\hat{S}_t = -\ln \hat{\rho}_t, \quad (1.7)$$

describing its quantum-mechanical nature—this definition being made due to the fact that its expectation value $S_t = \langle \hat{S}_t \rangle$ agrees with the equilibrium value successfully described by the von Neumann entropy (1.1) when the statistical state is of

equilibrium—and then to apply the principle of uniformity on this to arrive at its thermodynamic nature

$$\hat{\mathcal{S}}_{\mathcal{T}} = \mathcal{T} \hat{S}_t. \quad (1.8)$$

Starting from the necessary condition in scenario 2, we have then arrived to the conclusion that the problem of identifying a satisfactory expression for the thermodynamic entropy out of equilibrium should be pursued using scenario 1, the corresponding thermodynamic entropy $\mathcal{S}_{\mathcal{T}} = \langle \hat{\mathcal{S}}_{\mathcal{T}} \rangle$ being of the form

$$\mathcal{S}_{\mathcal{T}} = -\text{Tr}(\hat{\rho}_t \mathcal{T} \ln \hat{\rho}_t), \quad (1.9)$$

after identifying the appropriate transformation \mathcal{T} . This is clearly a functional not of the form $-\text{Tr}(\cdot \ln \cdot)$ applied on the density matrix $\hat{\rho}_t$, but of the form $-\text{Tr}(\cdot \mathcal{T} \ln \cdot)$, whose properties will be studied in detail in chapter 2. It is the aim of the next section to shed light on how \mathcal{T} has been identified in the past.

1.1 Irreversibility in quantum statistics

The first investigations of irreversibility within the quantum theory were initiated by Pauli (1928) in the same spirit as Boltzmann did in the classical theory, that is, understanding irreversibility as the realization of conditions which make the equation of motion for the occupation probabilities of the microscopic states—this equation being derived from (1.2)—attain a steady-state solution corresponding to the onset of thermalization if the system is left to evolve on its own from a nonequilibrium initial state.

More specifically, by imagining the approach to the steady state to be produced by a perturbation \hat{V} in the Hamiltonian $\hat{H} = \hat{\mathcal{H}} + \hat{V}$ of the system, small enough to ensure that the transition rates $W_{\alpha\beta}$ between the stationary states $\{|\alpha\rangle\}$ of the *unperturbed*

Hamiltonian $\hat{\mathcal{H}}$ —the bold notation denoting multiple quantum numbers—can be calculated using first-order time-dependent perturbation theory, then the occupation probabilities of these stationary states were shown by Pauli to satisfy

$$\frac{dP_{\alpha}}{dt} = \sum_{\beta} (W_{\alpha\beta}P_{\beta} - W_{\beta\alpha}P_{\alpha}), \quad (1.10)$$

which evidently admit steady-state solutions corresponding to the detailed balance $W_{\alpha\beta}P_{\beta} = W_{\beta\alpha}P_{\alpha}$ of all the quantum transitions allowed by the perturbation \hat{V} . The argument used, however, is based on the assumption that the density matrix is diagonal in the eigenbasis of the unperturbed Hamiltonian or, equivalently, that the coefficients of the total wavefunction expanded with respect to this eigenbasis have randomly distributed phases *at all times*.

This assumption, which is clearly unsatisfactory due to the arbitrary incorporation of elements not inherent to the dynamics of the system, has the same pathology as Boltzmann’s molecular chaos hypothesis in the classical theory of gases—where the molecules, after undergoing binary collisions, do not “remember” their velocities before the collisions—this hypothesis being needed to demonstrate the achievement of the equilibrium Maxwell-Boltzmann velocity distribution of the molecules as the steady-state solution of kinetic equations of the mathematical form of (1.10).

A significant improvement on the identification of conditions leading to equations like (1.10) with the minimum number of assumptions, and without compromising the inherent dynamics of the system, was first made with the independent works of [Van Hove \(1955b, 1957\)](#) and [Prigogine and Résibois \(1961\)](#), who derived equations from (1.2)—the so called generalized master equations—valid to *all* orders of time-dependent perturbation theory on \hat{V} .

It was shown that the random phase assumption was only necessary at the *initial* time of the evolution, a condition which is typically met for systems which are initially

prepared in a state of thermal *equilibrium*, represented by a diagonal density matrix in the eigenbasis of the unperturbed Hamiltonian. The root of irreversible behavior was then traced to the property of many-body systems of being very large (in the thermodynamic limit, infinitely large) leading to continuous quantum numbers; and to the property of the corresponding perturbations \hat{V} of extending over the whole system (e.g. the electron-phonon interaction), leading to the so-called *diagonal singularity*, which in condensed-matter systems produces dissipation, whereas in the interacting quantum fields of the elementary particles produces cloud effects [Van Hove \(1955a, 1956\)](#).

The language of generalized master equations became popular in nonequilibrium statistical mechanics by the early 1960's, thanks to the works of [Nakajima \(1958\)](#), [Zwanzig \(1960, 1964\)](#), [Fujita \(1962\)](#), [Mori \(1965\)](#), among others, who unified the seemingly different approaches to the problem of irreversibility in quantum many-body systems. In this formalism, there is a part $\hat{\varrho}_t = \mathcal{T}\hat{\rho}_t$ of the density matrix $\hat{\rho}_t$ of an isolated quantum system which suffices to explain the thermodynamic state at each moment in time, and a part $\hat{\rho}_t^\sim = (1 - \mathcal{T})\hat{\rho}_t$ containing only information about fluctuations and noise.

The generalized master equation is an equation of motion for the “relevant” part, obtained from (1.2), without approximations, by considering \mathcal{T} as a projection operator splitting the density matrix as

$$\hat{\rho}_t = \mathcal{T}\hat{\rho}_t + (1 - \mathcal{T})\hat{\rho}_t = \hat{\varrho}_t + \hat{\rho}_t^\sim, \quad (1.11)$$

and finding the coupled equations of motion for $\hat{\varrho}_t$ and $\hat{\rho}_t^\sim$. The relevant part can be easily shown to satisfy

$$i\frac{\partial\hat{\varrho}_t}{\partial t} = \mathcal{T}L\hat{\varrho}_t + \mathcal{T}Le^{-it(1-\mathcal{T})L}\hat{\rho}_0^\sim - i\int_0^t d\tau K_{t-\tau}\hat{\varrho}_\tau, \quad (1.12)$$

where the memory kernel $K_\tau = \mathcal{T}L e^{-i\tau(1-\mathcal{T})L}(1-\mathcal{T})L$ acts on the history of states described by $\hat{\rho}_\tau$ for $\tau < t$ and “propagates” their aggregate contribution to the rate of change of $\hat{\rho}_t$ at the present time.

The description of the approach to equilibrium in quantum statistics is obtained in this framework when the transformation \mathcal{T} is chosen as

$$\mathcal{T} = \mathcal{D}, \quad \text{where} \quad (\mathcal{D}\hat{A})|\alpha\rangle = A_{\alpha\alpha}|\alpha\rangle, \quad (1.13)$$

for any quantum observable \hat{A} , and $|\alpha\rangle$ being, as before, the eigenstates of the unperturbed Hamiltonian, that is, the transformation \mathcal{D} projects operators to their *diagonal* part with respect to this eigenbasis.

In particular, Van Hove’s results [Van Hove \(1955b, 1957\)](#) are obtained when the initial density matrix is diagonal—making $\hat{\rho}_0^\sim = 0$ in (1.12)—and the Pauli master equation (1.10) derived by subsequently taking the matrix elements of (1.12) in the $|\alpha\rangle$ -representation and assuming the perturbation \hat{V} to be weak enough and to act over sufficiently long times that the memory effects become negligible. The precise way in which this takes place has been proved to the highest mathematical sophistication by [Davies \(1974\)](#).

1.2 Nonequilibrium entropy in quantum statistics

As discussed in the previous section, the theory of irreversibility in quantum statistical mechanics has grown from a substantial amount of research on the approach to steady-state solutions of the occupation probabilities of the stationary states of a many-body system, which is brought to nonequilibrium situations by a perturbation \hat{V} . In thermodynamics, however, irreversibility is usually connected to the increasing of the thermodynamic entropy during a non-adiabatic evolution of the system. Let

us briefly review some of the previous approaches and compare with our approach in this thesis.

1.2.1 Previous approaches

Since the second law of thermodynamics is of such a general nature, it has been more complicated to come up with a unified quantum-mechanical expression for the nonequilibrium thermodynamic entropy since, in principle, any non-decreasing functional of the density matrix, which agrees with the thermodynamic entropy in equilibrium situations, would seem to be a good candidate. For this reason, there has been a handful of investigations searching for this kind of functionals. For a review of approaches up to 1979, the reader is referred to [Penrose \(1979\)](#).

We consider the thermodynamic entropy as directly related to heat, as originally conceived by Clausius, so here we briefly review only *some* of the works which have become well-known in the modern literature, which discuss a given expression for the nonequilibrium entropy together with the associated heat evolution. Note that we use the same notation S_t for the different expressions of entropy ($k_B = 1$), unless it is completely necessary to adopt a different one.

Jaynes

In order to better understand the trend of arguments in the subsequent discussion, it is illustrative to mention Jaynes' interpretation of the entropy [Jaynes \(1957a,b\)](#) as a *subjective* entity related to our ignorance of the probability distribution of the microscopic states of the system at a given time, when only the expectation values of the operators $\hat{F}_1, \hat{F}_2, \dots, \hat{F}_m$ are known.

The density matrix $\hat{\rho}$ which represents the *most unbiased* determination of the state of the system is then the one which maximizes the entropy $S = -\text{Tr}(\hat{\rho} \ln \hat{\rho})$

conditional on the information at hand, or the one which unconditionally maximizes

$$S - \lambda_1 \langle \hat{F}_1 \rangle - \lambda_2 \langle \hat{F}_2 \rangle - \cdots - \lambda_m \langle \hat{F}_m \rangle,$$

with the $\lambda_1, \dots, \lambda_m$ being Lagrange multipliers. The maximum-entropy density matrix is then obtained as

$$\hat{\rho} = \exp(-\lambda_0 \hat{1} - \lambda_1 \hat{F}_1 - \cdots - \lambda_m \hat{F}_m), \quad (1.14)$$

where $\lambda_0 = \ln Z(\lambda_1, \dots, \lambda_m) = \ln \text{Tr} \exp(-\lambda_1 \hat{F}_1 - \cdots - \lambda_m \hat{F}_m)$; the corresponding value of the entropy being

$$S = \lambda_0 + \lambda_1 \langle \hat{F}_1 \rangle + \cdots + \lambda_m \langle \hat{F}_m \rangle. \quad (1.15)$$

The way in which an infinitesimal amount of heat is considered in this formulation is by making an arbitrary infinitesimal variation of the inference problem, which consists of changing the previously known inputs $\hat{F}_1, \dots, \hat{F}_m$ and their expectation values $\langle \hat{F}_1 \rangle, \dots, \langle \hat{F}_m \rangle$ by the infinitesimal amounts $\delta \hat{F}_1, \dots, \delta \hat{F}_m$ and $\delta \langle \hat{F}_1 \rangle, \dots, \delta \langle \hat{F}_m \rangle$ in such a way that $\langle \delta \hat{F}_k \rangle$ and $\delta \langle \hat{F}_i \rangle$ are independent for all i and k . Calculating the maximum-entropy density matrix in this new situation yields the infinitesimal variation of the maximum entropy

$$\delta S = \lambda_1 \delta Q_1 + \cdots + \lambda_m \delta Q_m, \quad (1.16)$$

where $\delta Q_k = \delta \langle \hat{F}_k \rangle - \langle \delta \hat{F}_k \rangle$ is a generalization of the notion of infinitesimal heat (of the k^{th} type) applied to the system, since in the case in which only the average of the energy operator \hat{F}_1 is known, the associated lagrange multiplier is the inverse temperature $\lambda_1 = 1/T$ and (1.16) reduces to the known thermodynamic relation between infinitesimal entropy changes and heat.

We have omitted the time argument intentionally to emphasize that this is how we would determine the density matrix and entropy of a system in a situation where nothing else is known about it at a given moment in time, apart from the identification of the measurable quantities $\hat{F}_1, \hat{F}_2, \dots, \hat{F}_m$ and the knowledge of their expectation values. This situation is encountered in thermal equilibrium, with $Z(\lambda_1, \dots, \lambda_m)$ being the partition function, and the thermodynamic variables being related as

$$\langle \hat{F}_k \rangle = -\frac{\partial \lambda_0}{\partial \lambda_k}, \quad \lambda_k = \frac{\partial S}{\partial \langle \hat{F}_k \rangle}.$$

If the conditions of the system evolve in time—possibly from an initial thermal state as above—under the action of a possibly time-dependent perturbation \hat{V}_t in the Hamiltonian $\hat{H}_t = \hat{\mathcal{H}} + \hat{V}_t$ so that

$$i\frac{\partial \hat{\rho}_t}{\partial t} = [\hat{H}_t, \hat{\rho}_t] \equiv L_t \hat{\rho}_t, \quad (1.17)$$

then we have discussed that the entropy $S_t = -\text{Tr}(\hat{\rho}_t \ln \hat{\rho}_t)$ is unchanged due to the unitary nature of the time evolution. The way Jaynes introduces irreversibility is subjective, coming from our ignorance of the actual operator \hat{V}_t . By assigning probabilities p_γ to the different possibilities $\hat{V}_t^{(\gamma)}$, the resulting time-evolved density matrix does not follow a unitary evolution and the entropy S_t can be proved to increase. This is however a similar kind of argument to that used by Pauli—not inherent to the dynamics of the system—and therefore we will disregard it.

Robertson

A more objective view of the program initiated by Jaynes was undertaken by his doctoral student [Robertson \(1966\)](#) at Stanford. In Robertson's formulation, the entropy is defined as

$$S_t = -\text{Tr}(\hat{\sigma}_t \ln \hat{\sigma}_t), \quad (1.18)$$

where $\hat{\sigma}_t$ is a generalized canonical density operator

$$\hat{\sigma}_t = \exp\left[-\lambda_0(t) - \sum_n \int d\mathbf{r} \lambda_n(\mathbf{r}, t) \hat{F}_n(\mathbf{r})\right], \quad (1.19)$$

which reduces to Gibbs' canonical and grand-canonical densities when the thermodynamic coordinates represented, in general, by the operators $\hat{F}_n(\mathbf{r})$ —e.g. energy density, particle density, magnetization per unit volume, etc.—and the conjugate intensive parameters represented, in general, by $\lambda_n(\mathbf{r}, t)$, become independent of the position \mathbf{r} and time t , with \hat{F}_1 being the total Hamiltonian of the system and \hat{F}_2 the total number of particles.

The operators $\hat{F}_n(\mathbf{r})$, with $n = 1, 2, \dots, m$, represent the *macroscopically* observed variables in a given problem, using the same notation as Jaynes' in the previous section, and the $\lambda_0(t)$ and $\lambda_n(\mathbf{r}, t)$ are obtained from the $m + 1$ equations

$$\langle \hat{F}_n(\mathbf{r}) \rangle_t = \text{Tr} [\hat{F}_n(\mathbf{r}) \hat{\sigma}_t] = \text{Tr} [\hat{F}_n(\mathbf{r}) \hat{\rho}_t], \quad (1.20)$$

$$\text{Tr} (\hat{\sigma}_t) = 1. \quad (1.21)$$

where $\hat{\rho}_t$ is the density matrix of the system. The formulation is then equivalent to mapping a nonequilibrium problem described by $\hat{\rho}_t$ to a “local equilibrium” problem described by $\hat{\sigma}_t$ with the values of the intensive parameters $\lambda_0(t)$ and $\lambda_n(\mathbf{r}, t)$ —local time-dependent temperatures, chemical potential, etc.—chosen to capture the nonequilibrium situation at every moment of time.

Memory of past thermodynamic conditions enters Robertson's formulation by means of the equation of motion he derived for $\hat{\sigma}_t$

$$\frac{\partial \hat{\sigma}_t}{\partial t} = -iP_t L_t \hat{\sigma}_t - \int_0^t d\tau \mathcal{K}_{t,\tau} \hat{\sigma}_\tau, \quad (1.22)$$

with $\mathcal{K}_{t,\tau} = P_t L_t T_{t,\tau} (1 - P_\tau) L_\tau$. Here P_t and $T_{t,\tau}$ are both linear operators *depending*

on $\hat{\sigma}_t$, with $T_{t,\tau}$ satisfying $\partial T_{t,\tau}/\partial\tau = iT_{t,\tau}(1 - P_\tau)L_\tau$, and L_t defined in (1.17). This can be seen from the definition of how P_t acts on an arbitrary operator \hat{A}

$$P_t\hat{A} = \sum_n \int d\mathbf{r} \frac{\delta\hat{\sigma}_t}{\delta\langle\hat{F}_n(\mathbf{r})\rangle_t} \text{Tr}[F_n(\mathbf{r})\hat{A}],$$

with δ representing functional derivatives.

That both P_t and $T_{t,\tau}$ depend on $\hat{\sigma}_t$ implies that (1.22) is a *nonlinear* integro-differential equation leading, together with (1.19), (1.20), (1.21), and after defining

$$R_{nn'}(\mathbf{r}, \mathbf{r}'; t, \tau) = - \int_0^1 dx \text{Tr} \{ [iL_t\hat{F}_n(\mathbf{r})] T_{t,\tau} [1 - P_\tau] \hat{\sigma}_\tau^x [iL_\tau\hat{F}_n(\mathbf{r}')] \hat{\sigma}_\tau^{1-x} \},$$

to $2m$ coupled, nonlinear, integral and integro-differential equations

$$\frac{\partial\langle\hat{F}_n(\mathbf{r})\rangle_t}{\partial t} = \text{Tr} \{ [iL_t\hat{F}_n(\mathbf{r})]\hat{\sigma}_t \} + \sum_{n'} \int_0^t d\tau \int d\mathbf{r}' R_{nn'}(\mathbf{r}, \mathbf{r}'; t, \tau) \lambda_{n'}(\mathbf{r}', \tau) \quad (1.23)$$

in the $2m$ unknowns $\langle\hat{F}_n(\mathbf{r})\rangle_t$ and $\lambda_n(\mathbf{r}, t)$, whose solutions determine the entropy as

$$S_t = \lambda_0(t) + \sum_n \int d\mathbf{r} \lambda_n(\mathbf{r}, t) \langle\hat{F}_n(\mathbf{r})\rangle_t, \quad (1.24)$$

which is a generalization of Jaynes' result (1.15).

Robertson relates the nonequilibrium entropy (1.24) with heat in an irreversible process followed by the system as

$$S_t = S_0 + \int_{\text{rev}} dQ/T,$$

where dQ is an amount of heat imagined to enter the system (being isolated) when the original irreversible change is *replaced* by an equivalent imaginary reversible change, with the $\langle\hat{F}_n(\mathbf{r})\rangle_t$ and $\lambda_n(\mathbf{r}, t)$ chosen in such a way that this replacement be math-

ematically consistent. We shall see later that the nonequilibrium thermodynamic entropy defined in this work is more general than Robertson's and is more clearly connected with heat dissipation, without the need of such an imaginary replacement of the dynamics of the system.

McLennan-Zubarev-Hershfield

The operators (1.14) and (1.19) constitute density operators for local-equilibrium ensembles of the Gibbs form. Early attempts by McLennan (1963), for classical systems, and by Zubarev (1994) for classical and quantum systems, have been made to construct Gibbs-like ensembles for nonequilibrium steady states in terms of the forces which sustain the deviation from equilibrium.

In the McLennan-Zubarev formulation, the purpose is to construct a Gibbs-like density matrix (so-called statistical operator) by solving an equation of motion with the appropriate nonequilibrium boundary conditions breaking the time-reversal invariance associated with a closed system. In a system with N independent parts, each having a Hamiltonian \hat{H}_j , with $j = 1, \dots, N$, an inverse temperature β_j , a number of particles \hat{N}_j^λ of the λ^{th} species, at the chemical potential μ_j^λ , the McLennan-Zubarev form of the statistical operator is

$$\hat{\rho}_{t,\varepsilon} = \frac{1}{Z} \exp \left\{ - \sum_j \beta_j \left[\hat{H}_j - \sum_\lambda \mu_j^\lambda \hat{N}_j^\lambda \right] - \int_{-\infty}^0 d\tau e^{\varepsilon(\tau-t)} \hat{J}_S(\tau-t) \right\}, \quad (1.25)$$

where $Z = \text{Tr}(\hat{\rho}_{t,\varepsilon})$ is the normalization factor, and $\hat{J}_S(\tau) = \sum_j \beta_j \hat{J}_j^q(\tau)$ is the quantum-mechanical operator for the *classical* rate of change of the entropy or entropy production rate $dS/dt = \sum_j \beta_j dQ_j/dt$. That is, $\hat{J}_S(\tau)$ has the form of an entropy production operator if the heat flow to the j^{th} subsystem is defined as

$$\hat{J}_j^q(\tau) = \frac{d}{d\tau} \left[\hat{H}_j(\tau) - \sum_\lambda \mu_j^\lambda \hat{N}_j^\lambda(\tau) \right]. \quad (1.26)$$

In (1.25), a convergence factor $e^{\varepsilon\tau}$ is introduced in the time integral, with $\varepsilon \rightarrow 0^+$ after all calculations are done; and the operators in (1.26) are written in the Heisenberg representation, $\hat{H}_j(\tau) = e^{i\hat{H}\tau}\hat{H}_je^{-i\hat{H}\tau}$ and $\hat{N}_j^\lambda(\tau) = e^{i\hat{H}\tau}\hat{N}_j^\lambda e^{-i\hat{H}\tau}$, with respect to the total Hamiltonian $\hat{H} = \sum_j \hat{H}_j + \hat{V}$, with \hat{V} being the energy of interaction of the independent parts.

An alternative reformulation of nonequilibrium quantum-statistical mechanics for steady-state problems was done by Hershfield (1993), which has proved recently to be adequate for nonequilibrium quantum transport problems Dutt et al. (2011). In this formulation, the statistical operator is obtained as

$$\hat{\rho}_H = \exp(\hat{H} - \hat{Y}), \quad (1.27)$$

where $\hat{H} = \hat{\mathcal{H}} + e^{\varepsilon t}\hat{V}$ is the total Hamiltonian of the system, with \hat{V} being the perturbation driving the system out of equilibrium—also containing the interaction between the particles. The operator $\hat{Y} = \sum_{n=0}^{\infty} \hat{Y}_n$ is calculated recursively

$$[\hat{\mathcal{H}}, \hat{Y}_n] - i\varepsilon \hat{Y}_n = [\hat{Y}_{n-1}, \hat{V}],$$

with a $\hat{Y}_0 = \sum_{j,\lambda} \mu_j^\lambda \hat{N}_j^\lambda$ which does not commute with \hat{V} , making (1.27) a fully nonequilibrium statistical operator but with an equilibrium-like form, with which the calculation of expectation values of observables $\langle \hat{A} \rangle = \text{Tr}(\hat{\rho}_H \hat{A}) / \text{Tr}(\hat{\rho}_H)$ resembles that of equilibrium quantum-statistical mechanics. This is because the operator \hat{Y} commutes with the total Hamiltonian \hat{H} in the limit of adiabatic switching on of the perturbation ($\varepsilon \rightarrow 0^+$). Irreversibility enters this formulation in the form of assuming the decay of certain time-correlation functions without referring to the actual mechanism causing this decay.

It has been shown recently Ness (2013) that Hershfield's density matrix (1.27) is actually a particular case of the McLennan-Zubarev form of the nonequilibrium

statistical operator, so we can concentrate our discussion only on (1.25). An important observation is that, contrary to Robertson’s quasi-equilibrium density matrix (1.19), the exponent of the McLennan-Zubarev statistical operator (1.25) contains memory. The origin of this memory can be understood by relating the two formulations as

$$\hat{\rho}_{t,\varepsilon} = \exp\left(\mathcal{I}_H^\varepsilon \ln \hat{\sigma}_t\right), \quad (1.28)$$

where (1.25) is written in the particular case of operators $\hat{F}_n(\mathbf{r})$ in the spatially-continuous description corresponding only to \hat{N}_j^λ and \hat{H}_j in a spatially-discrete description. Here $\mathcal{I}_H^\varepsilon$ is an operator extracting the invariant part—with respect to \hat{H} —of its argument

$$\mathcal{I}_H^\varepsilon \hat{A}_t = \int_{-\infty}^0 d\tau e^{\varepsilon(\tau-t)} \hat{A}(\tau - t),$$

that is, it selects the zero-frequency component of the operator \hat{A}_t evolving in the Schrödinger picture after the Heisenberg picture is taken and Abel’s theorem is used ($\varepsilon \rightarrow 0^+$). Note that $\mathcal{I}_H^\varepsilon$, with the unperturbed Hamiltonian $\hat{\mathcal{H}}$ used instead of the total Hamiltonian \hat{H} —that is, taking the interaction picture—corresponds to \mathcal{D} in (1.13) Kubo (1957).

Memory thus enters the McLennan-Zubarev formulation as a result of manually breaking the time reversal of the von Neumann equation (1.2) for $\ln \hat{\rho}_t$

$$i \frac{\partial}{\partial t} \ln \hat{\rho}_t + [\ln \hat{\rho}_t, \hat{H}] = 0, \quad (1.29)$$

by adding the ε -dependent term $-\varepsilon (\ln \hat{\rho}_t - \ln \hat{\sigma}_t)$ on the right-hand side, after which $\hat{\rho}_t \rightarrow \hat{\rho}_{t,\varepsilon}$. This memory is however not manifested in the entropy, since Zubarev defined it the same way as Robertson did, as the expectation value of the “entropy operator” associated with the local equilibrium ensemble density

$$\hat{S}_t^{\text{loc}} = -\ln \hat{\sigma}_t, \quad (1.30)$$

calculated self-consistently as in (1.20)

$$S_t = \langle \hat{S}_t^{\text{loc}} \rangle = -\text{Tr}(\hat{\sigma}_t \ln \hat{\sigma}_t) = -\text{Tr}(\hat{\rho}_t \ln \hat{\sigma}_t).$$

Suzuki

Suzuki (2011, 2012) has found a general, Zubarev-type, expression for the nonequilibrium density matrix solving (1.17), by considering the particular case of an initial thermal equilibrium ensemble $\hat{\rho}_0 = \exp(-\beta \hat{\mathcal{H}})/Z_0(\beta)$ at inverse temperature β —with $Z_0(\beta) = \text{Tr} \exp(-\beta \hat{\mathcal{H}})$ —which at time t_0 is taken out of equilibrium by a perturbation \hat{V}_t , the total Hamiltonian being $\hat{H}_t = \hat{\mathcal{H}} + \hat{V}_t$, which generates a unitary time evolution described by the time-evolution operator satisfying the Schrödinger equation

$$i \frac{\partial}{\partial t} \hat{U}(t, t_0) = \hat{H}_t \hat{U}(t, t_0).$$

This nonequilibrium density matrix can be written as

$$\begin{aligned} \hat{\rho}_t &= \hat{U}(t, t_0) \hat{\rho}_0 \hat{U}^{-1}(t, t_0) = \frac{1}{Z_0(\beta)} \exp \left[-\beta \hat{U}(t, t_0) \hat{\mathcal{H}} \hat{U}^{-1}(t, t_0) \right] \\ &= \frac{1}{Z_0(\beta)} \exp \left[-\beta (\hat{\mathcal{H}} + \hat{R}(t, t_0)) \right], \end{aligned} \quad (1.31)$$

where the nonequilibrium operator $\hat{R}(t, t_0)$ satisfies the time evolution equation

$$i \frac{\partial}{\partial t} \hat{R}(t, t_0) = [\hat{H}_t, \hat{R}(t, t_0)] + [\hat{V}_t, \hat{\mathcal{H}}],$$

whose formal solution is evidently

$$\hat{R}(t, t_0) = i \int_{t_0}^t d\tau \hat{U}(t, \tau) [\hat{V}_\tau, \hat{\mathcal{H}}] \hat{U}^{-1}(t, \tau). \quad (1.32)$$

Suzuki has shown that (1.31) resums the perturbative expansion of the nonequilibrium density matrix developed by Kubo (1957). Furthermore, he has shown that the McLennan-Zubarev form of the statistical operator is obtained when a linear approximation to (1.32) with respect to the perturbation \hat{V}_t —this perturbation turned on adiabatically at a rate $\varepsilon \rightarrow 0^+$ —is made in the limit $t_0 \rightarrow -\infty$, and the resulting $\hat{R}(t, -\infty)$ is plugged back in (1.31).

A theory of entropy production in transport phenomena was then constructed by assuming the entropy operator (1.30) associated with the local equilibrium density matrix, which in the present case reads $\hat{S} = -\ln \hat{\rho}_0 = \beta \hat{\mathcal{H}} + \ln Z_0(\beta)$, and defining the irreversible entropy production rate as

$$\left(\frac{dS}{dt}\right)_{\text{irrev}} = \frac{d}{dt} \langle \hat{S} \rangle_t = \beta \frac{d}{dt} \text{Tr}(\hat{\mathcal{H}} \hat{\rho}_t), \quad (1.33)$$

where it is shown that only the symmetric part of the nonequilibrium density matrix (1.31), with respect to the inversion of space or the fields applied to the system, contribute to (1.33), providing a way to derive the associated Joule heat.

Polkovnikov

Polkovnikov (2011) has studied the properties of the diagonal entropy

$$S_d = - \sum_n \rho_{nn} \ln \rho_{nn} \quad (1.34)$$

involving only the diagonal elements of the nonequilibrium density matrix $\hat{\rho}_t$ in the instantaneous energy representation, showing that it behaves consistently with the expectations from thermodynamics. A similar proposal was made much earlier by Tolman (1938) and Ter Haar (1954) according to Jaynes (1957b).

The diagonal entropy is a functional of the type $-\text{Tr}(\cdot \ln \cdot)$, as can be seen by writing (1.34) as $S_d = -\text{Tr}[(\mathcal{T} \hat{\rho}_t) \ln(\mathcal{T} \hat{\rho}_t)]$, with \mathcal{T} the operator projecting the non-

equilibrium density matrix to its diagonal part with respect to the instantaneous energy basis. Since its discussion by Polkovnikov to the present time, it has been studied substantially by many authors in different scenarios, and will play an important part in our developments.

Relative-entropy formulations

Finally, we mention here some works on the relative entropy and its relation with discussions of entropy production. The introduction of the relative entropy was done by [Shannon \(1948\)](#) in classical information theory and its consideration in nonequilibrium quantum-statistical mechanics was first done by [Lindblad \(1973, 1975\)](#), who showed that for Markovian systems—usually this is applied in the study of open quantum systems—satisfying the most general form of a Pauli-type master equation

$$\frac{d}{dt}\mathcal{P}\hat{\rho}_t = \lambda^2 \Theta \mathcal{P}\hat{\rho}_t, \quad (1.35)$$

with \mathcal{P} any projection operator, λ a constant, and Θ the generator of a dynamical semigroup, meaning that if $\mathcal{P}\hat{\rho}_0$ is non-negative and normalized so is $\mathcal{P}\hat{\rho}_t$ for all t , then the quantity

$$\text{Tr} \left\{ \mathcal{P}\hat{\rho}_t [\ln \mathcal{P}\hat{\rho}_t - \ln(\mathcal{P}\hat{\rho}_t)_{\text{eq}}] \right\}, \quad (1.36)$$

with $(\mathcal{P}\hat{\rho}_t)_{\text{eq}}$ being any equilibrium solution of (1.35)—i.e. satisfying $\Theta(\mathcal{P}\hat{\rho}_t)_{\text{eq}} = 0$ —is non-negative. A detailed discussion of such considerations for quantum systems *weakly* coupled to thermal reservoirs can be found in [Spohn and Lebowitz \(1978\)](#).

We follow here a more recent approach to entropy production using relative entropy [Esposito et al. \(2010\)](#), which does not assume weak coupling. In this formulation, a system with Hamiltonian \hat{H}_t^s is considered in contact with *independent* reservoirs with Hamiltonians \hat{H}_r ($r = 1, 2, \dots$), which are in thermal equilibrium

$\hat{\rho}_r(0) = \hat{\rho}_r^{\text{eq}}$ at inverse temperature β_r and initially uncorrelated with the system

$$\hat{\rho}_0 = \hat{\rho}_0^s \prod_r \hat{\rho}_r^{\text{eq}}. \quad (1.37)$$

The subsequent evolution of the total system follows the von Neumann equation (1.17) with total Hamiltonian

$$\hat{H}_t = \hat{H}_t^s + \sum_r \hat{H}_r + \hat{V}_t,$$

where \hat{V}_t couples all the subsystems. The entropy of the system is defined as

$$S_t^s = -\text{Tr}_s (\hat{\rho}_t^s \ln \hat{\rho}_t^s), \quad (1.38)$$

where $\hat{\rho}_t^s$ —reduced density matrix of the system—is obtained from $\hat{\rho}_t$ by tracing over the degrees of freedom of the reservoirs.

The key point of this formulation is the invariance of the entropy of the total system—considered isolated—under its unitary evolution. This leads, from (1.1), (1.4), and (1.37), to

$$-\text{Tr} (\hat{\rho}_t \ln \hat{\rho}_t) = -\text{Tr} (\hat{\rho}_0 \ln \hat{\rho}_0) = -\text{Tr}_s (\hat{\rho}_0^s \ln \hat{\rho}_0^s) - \sum_r \text{Tr}_r \hat{\rho}_r^{\text{eq}} \ln \hat{\rho}_r^{\text{eq}}. \quad (1.39)$$

This is used to write the entropy change of the system $\Delta S_t^s = S_t^s - S_0^s$ as

$$\Delta S_t^s = \Delta_i S_t^s + \Delta_e S_t^s, \quad (1.40)$$

which is split into an entropy flow

$$\Delta_e S_t^s = \sum_r \beta_r Q_t^r, \quad (1.41)$$

with the heat flowing from reservoir r being—the average calculated using the total density matrix

$$Q_t^r = \langle \hat{H}_r \rangle_0 - \langle \hat{H}_r \rangle_t, \quad (1.42)$$

and an entropy production

$$\Delta_i S_t^s = D \left[\hat{\rho}_t \parallel \hat{\rho}_t^s \prod_r \hat{\rho}_r^{\text{eq}} \right], \quad (1.43)$$

where use is made of the definition of relative entropy between two density matrices $\hat{\rho}$ and $\hat{\rho}'$ —compare with (1.36)

$$D[\hat{\rho} \parallel \hat{\rho}'] = \text{Tr} [\hat{\rho} (\ln \hat{\rho} - \ln \hat{\rho}')],$$

which, being positive and equal to zero when the two density matrices are equal, may be used as a measure of “distance” between the two density matrices.

In this formulation the entropy of the system is a functional of the form $-\text{Tr}(\cdot \ln \cdot)$, that is, it is obtained as $S_t^s = -\text{Tr}[(\mathcal{P}\hat{\rho}_t) \ln(\mathcal{P}\hat{\rho}_t)]$, where \mathcal{P} traces the total density matrix over the degrees of freedom of the reservoirs: $\hat{\rho}_t^s = \mathcal{P}\hat{\rho}_t$. The problem with the separation (1.40) is that, according to (1.39), all entropy changes in the individual subsystems are restricted to keep the entropy of the total system *constant*, which does not align with Clausius’ summarized statement of the second law of thermodynamics [Clausius \(1865\)](#), which says that the entropy of the universe—an isolated system—is increasing.

If the relative entropy was then a good candidate to study entropy production, it would have to produce a positive rate of change for an isolated system initially prepared in a thermal equilibrium state $\hat{\rho}^{\text{eq}}$ at inverse temperature β . That is

$$\frac{d}{dt} S_t^{\text{rel}} = \frac{d}{dt} D[\hat{\rho}_t \parallel \hat{\rho}^{\text{eq}}] \geq 0.$$

This is not however the case. Suzuki (2011) has shown that this rate of change, with $\hat{\rho}_t$ satisfying the von Neumann equation, vanishes.

1.2.2 The new approach in this thesis

In most of the formulations discussed above for isolated quantum systems, an entropy operator is defined with respect to the local equilibrium density matrix $\hat{\sigma}_t$

$$\hat{S}_t^{\text{loc}} = -\ln \hat{\sigma}_t, \quad (1.44)$$

and the nonequilibrium entropy is obtained by taking expectation value with respect to the time-evolved density matrix satisfying the von Neumann equation (or a modified version of it breaking time-reversal invariance).

What is special about (1.44) is that it is a linear combination (see e.g. the exponent of (1.19)) of *macroscopic* observables—the observables $\hat{F}_n(\mathbf{r})$ in Robertson’s formulation, whose properties he did not mention. As we will discuss in detail in chapter 2, a macroscopic or slowly varying observable is obtained by extracting the diagonal part of the quantum operator representing the observable with respect to the eigenbasis of the Hamiltonian $\hat{\mathcal{H}}$ of uncoupled subsystems. That is, for every quantum observable \hat{A} of a system, its macroscopic or thermodynamically measurable part is another operator given by $\hat{\mathcal{A}} = \mathcal{D}\hat{A}$, with \mathcal{D} defined in (1.13).

Once an appropriate definition of macroscopic observables is given, the entropy operator is defined, contrary to (1.44), with respect to the nonequilibrium density matrix instead of the local equilibrium one

$$\hat{S}_t = -\ln \hat{\rho}_t. \quad (1.45)$$

This is taken here as the quantum operator for the negative of Gibbs’ *index of proba-*

bility Gibbs (1902), which identifies the entropy function in terms of the logarithm of the ensemble density function—which evolves according to Liouville equation—and whose expectation value in equilibrium is the thermodynamic entropy.

Having recognized the quantum observable for entropy, we then introduce, according to what was said above, the corresponding macroscopic or thermodynamically measurable part

$$\hat{\mathcal{S}}_t = \mathcal{D}\hat{\mathcal{S}}_t = -\mathcal{D} \ln \hat{\rho}_t. \quad (1.46)$$

This is considered as the operator representing thermodynamic measurements of the nonequilibrium entropy. Its expectation value

$$\mathcal{S}_t = \langle \hat{\mathcal{S}}_t \rangle = \text{Tr}(\hat{\rho}_t \hat{\mathcal{S}}_t) = -\text{Tr}(\hat{\rho}_t \mathcal{D} \ln \hat{\rho}_t), \quad (1.47)$$

is then the thermodynamic entropy. Note that this is not a functional of the form $-\text{Tr}(\cdot \ln \cdot)$ but of the form $-\text{Tr}(\cdot \mathcal{D} \ln \cdot)$.

We prove rigorously in chapter 2 that $\mathcal{S}_t - \mathcal{S}_0 \geq 0$, with the equality holding for quasistatic transformations of the system, which is Clausius' statement of the second law of thermodynamics. Also \mathcal{S}_t is identically zero for density matrices describing a pure state, which is the state of a quantum system at zero temperature. This is consistent with the third law of thermodynamics. The first law of thermodynamics is also shown to be incorporated in our definition of \mathcal{S}_t . Moreover, in the special but important case where the total isolated system is divided into *uncorrelated* subsystems—e.g. a consequence of considering each of the subsystems in the thermodynamic limit— \mathcal{S}_t agrees with Polkovnikov's diagonal entropy (1.34). However, when correlations between the subsystems are taken into account, there are entropy-increasing processes generated by these correlations which are described by (1.47) but not captured by the diagonal entropy.

Starting from more general initial states of the form

$$\hat{\rho}_0 = \exp(-\hat{S}_0),$$

where \hat{S}_0 is the initial entropy operator—usually but not necessarily taken to be of the local equilibrium form (1.44)—our formalism generalizes Suzuki’s representation of the nonequilibrium density matrix (1.31), by noticing that

$$\hat{\rho}_t = \exp(-\hat{S}_t), \quad (1.48)$$

with the entropy operator then evolving according to

$$\hat{S}_t = U(t, t_0) \hat{S}_0 U^{-1}(t, t_0). \quad (1.49)$$

This is nothing but the statement that \hat{S}_t satisfies the von Neumann equation, as already recognized by Zubarev (see e.g. (1.29)).

In chapter 2 we then develop a theory of entropy production by studying the equation of motion followed by the thermodynamic entropy operator \hat{S}_t . It turns out that this is the point where a natural connection with the well-established theory of irreversibility in terms of generalized master equations arises. For \hat{S}_t satisfies the same equation as $\hat{\rho}_t$, and we said that $\hat{\varrho}_t = \mathcal{D}\hat{\rho}_t$ was the relevant part of the density matrix for describing thermodynamic irreversibility. This means that $\hat{S}_t = \mathcal{D}\hat{S}_t$ satisfies the *same* Nakajima-Zwanzing generalized master equation (1.12) satisfied by $\hat{\varrho}_t$

$$i \frac{\partial \hat{S}_t}{\partial t} = \mathcal{D}L\hat{S}_t + \mathcal{D}L e^{-it(1-\mathcal{D})L} \hat{S}_0^\sim - i \int_0^t d\tau K_{t-\tau} \hat{S}_\tau, \quad (1.50)$$

where $\hat{S}_0^\sim = (1 - \mathcal{D})\hat{S}_0$. This is our starting point to study the connection between the average entropy production rate in a subsystem of the isolated quantum system and the associated heat evolution. We show that the classical theory of entropy

production can be derived from (1.50) under appropriate limits.

The quantum theory of entropy production developed in this thesis is applied in chapter 2 to the problem of electrical conduction, where the Joule heat is derived from a first-principle calculation of electronic entropy production. Furthermore, in chapter 3, it is shown how the results of this theory can be used to understand and solve a long-standing puzzle in the simplest model in quantum optics describing light-atom interactions: the Jaynes-Cummings model.

Chapter 2

Theory of Entropy Production in Quantum Many-Body Systems

Most of this work is published as:

E. Solano-Carrillo and A. J. Millis, Theory of entropy production in quantum many-body systems, *Phys. Rev. B* **93**, 224305 (2016).

The actual published text is shown at the end of this chapter.

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2.1 Overview

In this chapter we define the entropy operator as the negative of the logarithm of the density matrix, give a prescription for extracting its thermodynamically measurable part, and discuss its dynamics. For an isolated system we derive the first, second and third laws of thermodynamics. For weakly-coupled subsystems of an isolated system, an expression for the long time limit of the expectation value of the rate of change of the thermodynamically measurable part of the entropy operator is derived and interpreted in terms of entropy production and entropy transport terms. The interpretation is justified by comparison to the known expression for the entropy production in an aged classical Markovian system with Gaussian fluctuations

and by a calculation of the current-induced entropy production in a conductor with electron-phonon scattering.

Our presentation is organized as follows: in section 2.3 we give a brief review of entropy production and the second law of thermodynamics as they manifest in phenomenological thermodynamics. In section 2.4 we discuss the local equilibrium assumption from a quantum perspective, as well as thermodynamic measurements and observables. We derive the first law of thermodynamics from an expression for the average rate of change of the thermodynamic entropy, which is shown to hold for *quasi-static* transformations or slow processes. This section, which mainly discusses how the foundations of the classical theory are to be understood quantum-mechanically, serves as a motivation to introduce the operator for the rate of change of the thermodynamic entropy for general isolated quantum systems of which possible reservoirs are part of.

A transition is made in section 2.5 to the generalized thermodynamic description of quantum systems. The second and third law of thermodynamics are established here for any isolated system, and an entropy balance equation is derived, splitting the average rate of change of the thermodynamic entropy into entropy production and entropy transport terms. In section 2.6, we show how the theory is consistent with Onsager's classical stochastic entropy production in an aged system. Finally, in section 2.7 we calculate the electronic entropy production in a simple metal consisting of independent electrons weakly coupled to phonons in the presence of an external electric field, deriving the Joule heating, and we conclude with section 2.8.

2.2 Introduction

Attempts to show how nonequilibrium thermodynamic behavior emerges from the underlying quantum mechanics of individual particles is now being dubbed quan-

tum thermodynamics [Gemmer et al. \(2004\)](#); [Millen and Xuereb \(2016\)](#); [Goold et al. \(2016\)](#); [Vinjanampathya and Anders \(2016\)](#). Several approaches have arisen, revealing important aspects in this endeavor, such as how thermal fluctuations and external driving mechanisms affect the stochastic course of nonequilibrium processes of small systems [Bustamante et al. \(2005\)](#) which has led to fluctuation theorems [Esposito et al. \(2009a\)](#); [Campisi et al. \(2011\)](#); [Dorner et al. \(2012\)](#) going beyond the results from the Kubo linear response theory, as well as generalized fluctuation-dissipation relations as studied in isolated quantum systems after a quench [Khatami et al. \(2013\)](#); [Maruzzi and Gambassi \(2014\)](#); [Essler et al. \(2012\)](#). Other aspects, more in the spirit of traditional nonequilibrium statistical mechanics [Penrose \(1979\)](#) include thermalization in isolated quantum systems [Polkovnikov et al. \(2011\)](#); [Yukalov \(2011\)](#); [D'Alessio et al. \(2016\)](#); [Gogolin and Eisert \(2016\)](#); [Eisert et al. \(2015\)](#), and the establishment of steady states in open quantum systems [Dutt et al. \(2011\)](#); [Esposito et al. \(2015\)](#); [Hsiang and Hu \(2015\)](#); [Yuge and Sugita \(2015\)](#); [Ness \(2014\)](#); [Manzano and Hurtado \(2014\)](#); [Xu and Cao \(2016\)](#). A unified treatment along the lines of the classical theory of nonequilibrium thermodynamics is of crucial importance for a clear identification of the quantum-to-classical correspondence and the new features brought about by fully quantum-mechanical nonequilibrium behavior.

The remarkable success of the classical theory [Prigogine \(1967\)](#); [de Groot and Mazur \(1984\)](#); [Jou et al. \(1999\)](#) in the description of macroscopic phenomena in fluids motivates us to ask what are the basic ingredients of this formalism that such a unified treatment of quantum thermodynamics must also contain. We remind that the building blocks of the classical theory are: (i) macroscopic observables, explicitly defined as a set of thermodynamically measurable or slowly-varying quantities, (ii) conservation laws for these variables and, as a foundational pillar, (iii) an entropy balance equation is established, splitting the rate of change of entropy as a part which is irreversibly produced, in accordance with the second law of thermodynamics, and

a part which is transported. The validity of this theory relies on the *local equilibrium* assumption, whereby the nonequilibrium thermodynamic entropy is considered locally as a function of the same extensive variables as in equilibrium.

Although significant attempts to give a meaning to entropy out of equilibrium [Lieb and Yngvason \(2013\)](#) have long been known in quantum statistics [Mori \(1956, 1958\)](#); [Zubarev \(1994\)](#); [Robertson \(1966\)](#), a complete theory of quantum entropy production has not been provided yet. The main problem is how to conceive an adequate quantum entropy balance equation without assuming local equilibrium.

For an isolated system, there is no entropy to be transported outside the system and hence the entropy balance equation reduces to finding the right quantum expression for entropy whose rate of change is non-negative, according to the second law of thermodynamics, this rate then being the entropy production. Important efforts have been devoted to obtain such an expression from the density matrix [Penrose \(1979\)](#); [Polkovnikov \(2011\)](#); [Ikeda et al. \(2015\)](#), but the third law of thermodynamics, involving the vanishing entropy of pure states has not been satisfactorily established.

On the other hand, for a subsystem of an isolated system the establishment of a quantum entropy balance equation has been partially addressed [Spohn \(1978\)](#); [Spohn and Lebowitz \(1978\)](#); [Esposito et al. \(2010\)](#); [Hosseini-Nejad et al. \(2015\)](#); [Mehta and Andrei \(2008\)](#); [Suzuki \(2011, 2012\)](#) by assuming that the rate of change of an adopted expression for the nonequilibrium entropy of the subsystem, obtained from the reduced density matrix, is directly connected, as in the classical theory, with the rate of change of its energy. This involves the identification of a microscopic expression for heat which is not unique [Pucci et al. \(2013\)](#) and therefore quite problematic, but most importantly, does not constitute a full deviation from the local equilibrium assumption, as we show later.

The purpose of this chapter is to provide a more general treatment of quantum entropy production and then lay the foundation of a unified theory of quantum

thermodynamics in close correspondence with the classical theory. We introduce a *new* thermodynamic entropy operator $\hat{\mathcal{S}}_t$ for isolated quantum many-body systems and show that the rate of change of its expectation value is non-negative, according to the second law of thermodynamics. Unlike previous approaches, we establish the third law of thermodynamics as a well-defined vanishing of the thermodynamic entropy for pure states.

The quantum entropy balance equation for a given subsystem of an isolated system is obtained by first studying the time evolution of $\langle \partial_t \hat{\mathcal{S}}_t \rangle$ for the isolated system from first principles, i.e. from the Liouville-von Neumann equation for the density matrix, using the standard generalized master equation approach of nonequilibrium statistical mechanics [Van Hove \(1957\)](#); [Prigogine and Résibois \(1961\)](#); [Fujita \(1962\)](#); [Nakajima \(1958\)](#); [Zwanzig \(1960\)](#), and by subsequently making reasonable assumptions regarding the factorization properties of the nonequilibrium probability distribution of microscopic states over the degrees of freedom of the different subsystems.

We restrict here to weakly-coupled subsystems to show how our theory is consistent with the classical theory, to elucidate the manner in which the local equilibrium approximation can be fully abandoned, and to pave the way to study cases of strong coupling between subsystems for which the aforementioned factorization properties of the probability distribution of microscopic states become the main subject of study, marking a deep connection with quantum information theory. A detailed investigation of a new methodology to approach these cases will be considered elsewhere.

The pursue of the so outlined research program is essential both for a more fundamental understanding of nonequilibrium behavior [Jarzynski \(2015\)](#), and because entropy production is inherent to dissipation so that a good atomic-scale description may have technological impact, e.g. by enabling better control of waste heat and thermoelectric effects in single-molecule electronics [Aradhya and Venkataraman \(2013\)](#); [Lee et al. \(2013\)](#); [Pekola \(2015\)](#), guiding the efficient design of quantum refrigerators

Feldmann and Kosloff (2012) and quantum heat machines Uzdin et al. (2015), nano-sized photoelectric devices Rutten et al. (2009), nanothermoelectric engines Esposito et al. (2012, 2009b) based on quantum dots, etc., which are envisioned as practical applications of quantum thermodynamics.

It turns out, as we show here with a particular example of electronic conduction in the presence of phonon modes playing the role of a reservoir, that our theory gives an explicit expression for the Joule heating from a calculation of the steady state electronic entropy production alone. This represents an important progress since this is done without calculating the rate of change of the energy of the electron subsystem.

2.3 Entropy production in phenomenological thermodynamics

The thermodynamic definition of entropy *changes* for any kind of process in a closed system (not interchanging particles with the reservoirs) was given by Clausius at the very end of his monumental 1865 paper Clausius (1865); Cropper (1986). If the system, which is considered to be in contact with a set of heat sources at different temperatures T , follows a path γ in the space of thermodynamic states, joining the initial and final arbitrary states A and B , respectively, then the thermodynamic entropy change in the process is

$$\mathcal{S}_B - \mathcal{S}_A = N_C[\gamma] + \int_A^B (\dot{d}Q/T)_\gamma, \quad (2.1)$$

where $\dot{d}Q$ is an infinitesimal amount of heat absorbed from (or surrendered to) the heat source at temperature T , and the quantity $N_C[\gamma]$, representing what came to be known as the “uncompensated heat of Clausius” Velasco et al. (2011), is a functional

of the process. Clausius defined it in such a way that

$$N_C[\gamma] \equiv - \oint_{\gamma} \dot{d}Q/T = - \int_A^B (\dot{d}Q/T)_{\gamma} - \int_B^A (\dot{d}Q/T)_{\gamma_R}, \quad (2.2)$$

where γ_R is an arbitrary *reversible* path which is “imagined” to bring the system back to its initial state A . He proved that

$$N_C[\gamma] \geq 0, \quad (\text{Clausius' inequality}), \quad (2.3)$$

for any γ , which was a generalization of Carnot’s results for cyclic processes; the equality holding if and only if γ is a reversible path. This is the starting point of all the discussions found in textbooks of the second law of thermodynamics [Fermi \(1956\)](#) and is therefore regarded here as the fundamental expression for this law.

A classical formulation of nonequilibrium thermodynamics has been founded [Prigogine \(1967\)](#); [de Groot and Mazur \(1984\)](#) by taking as starting point (2.1) written in differential form and generalized to apply locally in small volume elements, δv , of a system

$$d\mathcal{S} = d_i\mathcal{S} + d_e\mathcal{S}, \quad (2.4)$$

where $d_i\mathcal{S} \equiv dN_C$ is the entropy produced, during an infinitesimal time interval, due to irreversible processes taking place inside the volume element, and $d_e\mathcal{S}$ the entropy supplied *from* its surroundings ($\equiv \dot{d}Q/T$ for a closed element). The second law of thermodynamics requires only that the entropy produced satisfies

$$d_i\mathcal{S} \geq 0, \quad (\text{Clausius' inequality}). \quad (2.5)$$

The theory so obtained for the phenomenological entropy production, $\Pi_{\delta v} = d_i\mathcal{S}/dt$, successfully describes *slow* processes or phenomena where the decay time of local perturbations is very short compared to the global relaxation time, as in chemical

reactions, diffusion processes, heat conduction, and their cross effects in gases and liquids. However, it requires fundamental modifications for *fast* processes [Jou et al. \(1999\)](#) and, in the following, we argue from a quantum-mechanical perspective why this happens to be the case, setting the stage and motivating the method for the subsequent development of our theory.

2.4 Local equilibrium and quasistatic quantum transformations

Consider an isolated macroscopic system, possibly containing a set of particle and heat reservoirs which is divided into macroscopic subsystems. Microscopically, the total system is defined by the Hamiltonian

$$\hat{H} = \sum_l \hat{H}_l + \sum_{l < m} \hat{H}_{lm}, \quad (2.6)$$

where \hat{H}_l is the Hamiltonian of subsystem l , involving the kinetic energies of the particles comprising the subsystem as well as the energy of interaction among all these particles; and \hat{H}_{lm} is the Hamiltonian representing the interactions among the particles of subsystem l with those of subsystem m , possibly including hopping terms allowing particle transfer.

The fundamental assumption of statistical mechanics [Landau and Lifshitz \(1980\)](#) is that, since the interaction energy among the parts scales with their common surface areas, while the energy of the parts scales with their respective volumes, we can then remove all \hat{H}_{lm} in (2.6) from a *macroscopic* description of the dynamics and introduce instead a set of time-dependent parameters $\{x_\lambda^l\}$ embodying macroscopic constraints for the subsystem l , that evolve in time due to changes in the other subsystems. The

operator representing macroscopic energy measurements in this approximation is

$$\hat{\mathcal{H}} = \sum_l \hat{\mathcal{H}}_l, \quad \text{with } \hat{\mathcal{H}}_l = \hat{H}_l(\{x_\lambda^l\}), \quad (2.7)$$

where the notation in (2.7) indicates that $\hat{\mathcal{H}}_l$ is to be taken as \hat{H}_l plus an external potential due to the other subsystems and represented *parametrically*. For instance, a quantum subsystem acted upon by an external electric field is seen in the description of (2.6) as having a Coulomb potential energy (operator) coupling all the charges of the subsystem with all the charges outside of it which are sources of this field, while in the approximate description of (2.7), it is seen as coupled to an external parameter \mathbf{E} representing the strength of the field. We shall call the latter the *thermodynamic* description.

The local equilibrium assumption in the thermodynamic description is the statement that the macroscopic state of each part of our system, with a number of particles operator $\hat{\mathcal{N}}_l$, a temperature T_l and a chemical potential μ_l , is an equilibrium state. The local equilibrium density matrix of the total system is the factorized Gibbs state (subsystems macroscopically uncorrelated)

$$\hat{\varrho}^r = \bigotimes_l \hat{\varrho}_l^r = \bigotimes_l \exp[-(\hat{\mathcal{H}}_l - \mu_l \hat{\mathcal{N}}_l - \Omega_l)/T_l], \quad (2.8)$$

with $\Omega_l = \Omega_l(T_l, \mu_l, \{x_\lambda^l\})$ the thermodynamic potential of subsystem l , introduced so as to normalize the density matrix, that is, $\text{Tr} \exp[-(\hat{\mathcal{H}}_l - \mu_l \hat{\mathcal{N}}_l)/T_l] = \exp(-\Omega_l/T_l)$. Note that, since the degrees of freedom of different subsystems are *uncoupled* in the thermodynamic description, all operators $\hat{\mathcal{H}}_l$ and $\hat{\mathcal{N}}_m$ form a mutually commuting set and then define a natural basis of common eigenstates that we represent as $\{|\boldsymbol{\alpha}\rangle\}$.

The appearance of this natural set defines a family of observables acting on the system Hilbert space that, like $\hat{\mathcal{H}}_l$ and $\hat{\mathcal{N}}_m$, we call thermodynamic; these observables

are diagonal in the basis $\{|\boldsymbol{\alpha}\rangle\}$. According to this, $\hat{\mathcal{H}}$ is a thermodynamic observable, and we denote the set of all these operators as

$$\mathcal{T} = \{\hat{\mathcal{A}} : [\hat{\mathcal{A}}, \hat{\mathcal{H}}] = 0\}. \quad (2.9)$$

Clearly all constant operators as well as all time-averaged observables [Kubo \(1957\)](#); [Zubarev \(1994\)](#) belong to this family. With \mathcal{D} denoting the projection operator to the subspace spanned by $\{|\boldsymbol{\alpha}\rangle\langle\boldsymbol{\alpha}|, \dots\}$, we can then split an arbitrary observable \hat{A} in the convenient form

$$\hat{A} = \mathcal{D}\hat{A} + \mathcal{N}\hat{A} = \hat{\mathcal{A}} + \hat{A}^\sim, \quad (2.10)$$

where $\hat{\mathcal{A}} = \mathcal{D}\hat{A}$ is the thermodynamically measurable part (or thermodynamic part) of \hat{A} ; the complementary part being $\hat{A}^\sim = \mathcal{N}\hat{A} = \hat{A} - \hat{\mathcal{A}}$.

The thermodynamic observables must have the characteristic of being slowly-varying quantities [Kirkwood \(1946\)](#); [Green \(1952\)](#); [Yamamoto \(1953\)](#); [Zwanzig \(1961\)](#). This is quantified in our theory by introducing a geometric measure, Δ , of how approximate is the thermodynamic description. For this, let us introduce for an arbitrary observable \hat{B} the hermitian operator

$$\hat{C}_{AB} = -i[\hat{\mathcal{A}}, \hat{B}] \quad \text{with} \quad \hat{\mathcal{A}} \in \mathcal{T}, \quad (2.11)$$

and consider the simple geometry induced by the Hilbert-Schmidt norm $\|\hat{C}_{AB}\| = (\text{Tr} \hat{C}_{AB}^\dagger \hat{C}_{AB})^{1/2}$. It is trivially seen that

$$\|\hat{C}_{\mathcal{H}0}\| = \|\hat{C}_{\mathcal{A}0}\| = 0, \quad (2.12)$$

and by using the Jacobi identity for commutators, together with $[\hat{\mathcal{A}}, \hat{\mathcal{H}}] = 0$, coming from (2.9), we can write

$$\|\hat{C}_{\mathcal{H}\hat{\mathcal{A}}}\| = \|\hat{C}_{\mathcal{A}\mathcal{H}\hat{\mathcal{A}}}\|, \quad (2.13)$$

where we identify $\dot{\hat{\mathcal{A}}} = \hat{C}_{AH}$ when the parameters representing external constraints are fixed in time. Therefore, if \hat{C}_{HH} tend to the null operator in the norm, i.e. if we have $\Delta \rightarrow 0$ with

$$\Delta^2 = \varepsilon_0^{-4} \|\hat{C}_{HH}\|^2 = \varepsilon_0^{-4} \sum_{\alpha\alpha'} (\varepsilon_\alpha - \varepsilon_{\alpha'})^2 |\langle \alpha | \hat{H} | \alpha' \rangle|^2, \quad (2.14)$$

where $\hat{\mathcal{H}}|\alpha\rangle = \varepsilon_\alpha|\alpha\rangle$ and ε_0 is the smallest characteristic energy in the system (making Δ dimensionless); then we conclude, by using (2.12), (2.13) as well as the continuity of the norm, that the quality of slow variation can be expressed as

$$\|\dot{\hat{\mathcal{A}}}\| = \|[\hat{\mathcal{A}}, \hat{H}]\| = O(\Delta). \quad (2.15)$$

The condition $\Delta \rightarrow 0$ is physically realized when the thermodynamic limit is taken for all the subsystems comprising the total system, since in this limit $\langle \hat{H} \rangle$ and $\langle \hat{\mathcal{H}} \rangle$ tend to be indistinguishable for arbitrary states.

2.4.1 Dynamical measurements and thermodynamic observables

We give now an alternative way to think about the macroscopic or thermodynamic observables (2.9). From an empirical point of view, the characteristic property of macroscopic observables is that they vary slowly in the scale of the time resolution Δt of the instruments measuring them Kirkwood (1946). These measurements are of a thermodynamic kind, when the dynamical fluctuations of the observable are negligibly small, as is the case for systems with many degrees of freedom when considered in the thermodynamic limit.

Clearly, the dynamical fluctuations of observables start playing an important role

for the length scales of mesoscopic measurements—in which they are of the brownian-motion type—and are completely prominent for microscopic measurements, in which the quantum interference of individual microstates displays substantial changes with time. Therefore, it is indispensable to define how a thermodynamic observable is to be understood in this quantum limit where the dynamical fluctuations are strong.

In order to achieve this, we translate the defining property of a classical macroscopic observable to the quantum regime. That is, a quantum-mechanical observable \hat{M} is macroscopic if it varies slowly in the time scale Δt of measurement. In the eigenbasis $\{|n\rangle\}$ of the total Hamiltonian \hat{H} of the system, with $\hat{H}|n\rangle = E_n|n\rangle$, its matrix elements then satisfy

$$|\dot{M}_{nm}| \Delta t \ll |M_{nm}| \quad (\text{Slowly changing matrix elements}). \quad (2.16)$$

Now, in the Heisenberg representation, the rate of change of this macroscopic observable is $i\dot{\hat{M}} = [\hat{M}, \hat{H}]$ which, after taking matrix elements in the eigenbasis $\{|n\rangle\}$, gives an equation for $|\dot{M}_{nm}|$. When this equation is substituted in (2.16), we arrive at the more useful inequality

$$|E_n - E_m| \Delta t \ll 1. \quad (2.17)$$

That the measurements are in the quantum regime implies that the experimental uncertainty in energy measurements ΔE is related to the time resolution Δt by the uncertainty principle $\Delta E \Delta t \sim 1$, which allows us to write (2.17) in the form

$$|E_n - E_m| \ll \Delta E. \quad (2.18)$$

The quality (2.16) of slowly changing matrix elements of a macroscopic observable then implies from (2.18) that \hat{M} has most of its matrix elements connecting states

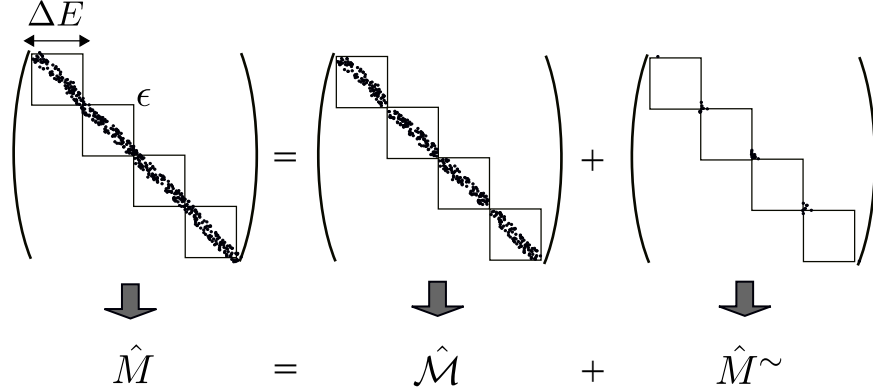


Figure 2.1: Matrix representation, in the energy basis, of a slowly varying macroscopic observable \hat{M} . The square blocks are ϵ -subspaces with a spread in energy, ΔE , given by the experimental uncertainty. The thermodynamically observable part, $\hat{\mathcal{M}}$, of the operator is constructed as explained in the text for a general quantum-mechanical observable \hat{A} .

with energies differing by quantities much smaller than the experimental uncertainty ΔE . This is shown in the upper left of Fig. 2.1 as a very narrow band of non-zero matrix elements along the main diagonal in the energy representation.

For systems with many degrees of freedom, macroscopic measurements do not discriminate between energy levels spaced within ΔE , so it is convenient to write the total Hamiltonian $\hat{H} = \sum_n E_n \hat{P}_{nn}$ in a way exploiting this experimental fact, where we have denoted the level projectors as $\hat{P}_{nm} = |n\rangle\langle m|$. For this, we introduce the new projectors $\hat{\mathcal{P}}_\epsilon(\Delta E) = \sum_{n, |E_n - E_\epsilon| \leq \Delta E} \hat{P}_{nn}$, where E_ϵ is an arbitrary energy eigenvalue within the interval ΔE which, for definiteness, is taken as the closest eigenvalue to the middle point of the interval. We then rewrite $\hat{H} = \hat{\hat{H}} + \hat{\tilde{H}}$, where $\hat{\hat{H}} = \sum_\epsilon E_\epsilon \hat{\mathcal{P}}_\epsilon(\Delta E)$ and $\hat{\tilde{H}} = \sum_\epsilon \sum_{n, |E_n - E_\epsilon| \leq \Delta E} (E_n - E_\epsilon) \hat{P}_{nn}$.

From the viewpoint of macroscopic observations of the internal energy of the system, it is clear that $\hat{\hat{H}}$ is way more relevant than $\hat{\tilde{H}}$ since, for a given energy level E_ϵ , we have $|E_\epsilon| \gg |E_n - E_\epsilon|$ for all energy levels n within the ϵ -block to which E_ϵ belongs, i.e. such that $|E_n - E_\epsilon| \leq \Delta E$. For this reason, we identify $\hat{\hat{H}}$ as the thermodynamic part of the energy observable. Note that the arbitrariness in the

selection of E_ϵ within the ϵ -block is removed in the truly quantum regime where individual energy levels can be resolved $\Delta E \sim \delta E$ —with δE being a typical energy level spacing—so that the ϵ -blocks attain their minimum size.

Following a prescription similar to that introduced by [Van Kampen \(1993\)](#), we describe now a way to define a complete set of thermodynamic observables, whose simultaneous measurements fully represent the quantum thermodynamic state. Since, by construction, the subspaces labeled by ϵ are mutually orthogonal, the completeness relation for the energy eigenstates is expressed as $\sum_\epsilon \hat{\mathcal{P}}_\epsilon = \hat{1}$ —regardless of the magnitude of ΔE , which is why we omit it as argument in the projector $\hat{\mathcal{P}}_\epsilon$.

Given a quantum observable \hat{A} , we can then decompose it as

$$\hat{A} = \sum_\epsilon \hat{\mathcal{P}}_\epsilon \hat{A} \hat{\mathcal{P}}_\epsilon + \sum_{\epsilon \neq \epsilon'} \hat{\mathcal{P}}_\epsilon \hat{A} \hat{\mathcal{P}}_{\epsilon'}. \quad (2.19)$$

This decomposition is shown in the upper part of [Fig. 2.1](#) (where each block is a different ϵ -subspace) in the special case of a macroscopic observable $\hat{A} = \hat{M}$, for which the second matrix in the sum is sparse outside the ϵ -blocks, as has been shown using the uncertainty principle.

Now proceed by diagonalizing \hat{A} in each of these subspaces separately, finding the eigenvalues $A_{\epsilon,a}$, which are the outcomes of all possible measurements of \hat{A} , and the eigenvectors $|\epsilon; a\rangle$, which define the projectors $\hat{P}_{\epsilon,aa'} = |\epsilon, a\rangle\langle\epsilon, a'|$. But observations of \hat{A} can be resolved within an uncertainty ΔA so, in analogy with the internal energy measurements, we need to construct new projectors $\hat{\mathcal{P}}_{\epsilon,\alpha}(\Delta A) = \sum_{a,|A_{\epsilon,a}-A_{\epsilon,\alpha}|\leq\Delta A} \hat{P}_{\epsilon,aa}$. With these, we can rewrite the quantum observable as $\hat{A} = \hat{A} + \hat{\hat{A}}$, where $\hat{\hat{A}} = \sum_{\epsilon,\alpha} A_{\epsilon,\alpha} \hat{\mathcal{P}}_{\epsilon,\alpha}(\Delta A)$ will be identified as the thermodynamically measurable part of the quantum observable \hat{A} , and $\hat{\hat{A}} = \hat{A} - \hat{\hat{A}}$.

By construction, the thermodynamically measurable part $\hat{\hat{A}}$ of \hat{A} commutes with \hat{H} (but not with \hat{H}). Following this procedure, we can add as much macroscopic

observables as needed to completely define the quantum thermodynamic state which, in terms of measurements, is described by the eigenvalues $\{\epsilon, \alpha, \beta, \dots\}$ of the mutually commuting set $\{\hat{H}, \hat{A}, \hat{B}, \dots\}$. This has to be done, however, in a way free of the arbitrariness introduced by the magnitude of ΔE , which can only be achieved in the truly quantum regime where $\Delta E \sim \delta E$.

To emphasize this, the operator \hat{H} representing macroscopic energy measurements in the quantum regime of observations is renamed $\hat{\mathcal{H}}$. In general, the thermodynamic part $\{\hat{A}, \hat{B}, \dots\}$ of the quantum observables $\{\hat{A}, \hat{B}, \dots\}$ is renamed, respectively, $\{\hat{\mathcal{A}}, \hat{\mathcal{B}}, \dots\}$ in this regime. These operators are diagonal in the common eigenbasis $\{|\epsilon, \alpha, \beta, \dots\rangle\}$ of the mutually commuting set $\{\hat{\mathcal{H}}, \hat{\mathcal{A}}, \hat{\mathcal{B}}, \dots\}$, which we rename $\{|\boldsymbol{\alpha}\rangle\}$. The the family of all such thermodynamic observables is nothing more but (2.9).

2.4.2 The first law of thermodynamics

We give now the steps that constitute our general method in the next section. Given the density matrix $\hat{\rho}_t$ of the total system, we define the entropy operator as the negative of its logarithm, $\hat{S}_t = -\ln \hat{\rho}_t$ and, from this and the aforementioned discussion, the *thermodynamic* entropy operator as $\hat{\mathcal{S}}_t = \mathcal{D}\hat{S}_t$. Since in the local equilibrium approximation the density matrix $\hat{\rho}_t = \hat{\rho}^r$ is already diagonal in the basis $\{|\boldsymbol{\alpha}\rangle\}$, we have in this case

$$\hat{\mathcal{S}}^r = -\ln \hat{\rho}^r = \frac{1}{T_l} \sum_l (\hat{\mathcal{H}}_l - \mu_l \hat{\mathcal{N}}_l - \Omega_l), \quad (2.20)$$

where we have used the commutativity of all $\hat{\mathcal{H}}_l$ and $\hat{\mathcal{N}}_m$ to express $\ln \hat{\rho}^r = \sum_l \ln \hat{\rho}_l^r$. We are interested in thermodynamic entropy changes as the main observable, then

the next step is an expression for $\langle \partial_t \hat{\mathcal{S}}_l \rangle$, which we get by first differentiating (2.20)

$$d\hat{\mathcal{S}}^r = \sum_l \frac{1}{T_l} [d\hat{\mathcal{H}}_l - d\mu_l \hat{\mathcal{N}}_l - \mu_l d\hat{\mathcal{N}}_l - d\Omega_l - \frac{dT_l}{T_l} (\hat{\mathcal{H}}_l - \mu_l \hat{\mathcal{N}}_l - \Omega_l)]. \quad (2.21)$$

Since Ω_l is a function of μ_l , T_l and of the external parameters, x_λ^l , implicit in $\hat{\mathcal{H}}_l$, we can differentiate the normalization relation $\text{Tr} \exp[-(\hat{\mathcal{H}}_l - \mu_l \hat{\mathcal{N}}_l)/T_l] = \exp(-\Omega_l/T_l)$ after variations in these arguments to get, after noting that $\langle \hat{G}_l \rangle = \text{Tr} \hat{\rho}^r \hat{G}_l = \text{Tr} \hat{\rho}_l^r \hat{G}_l$ for a local operator \hat{G}_l acting on the l -th subsystem,

$$d\Omega_l = - \sum_\lambda F_\lambda^l dx_\lambda^l - \langle \hat{\mathcal{N}}_l \rangle d\mu_l - \frac{dT_l}{T_l} (\langle \hat{\mathcal{H}}_l \rangle - \mu_l \langle \hat{\mathcal{N}}_l \rangle - \Omega_l), \quad (2.22)$$

with $F_\lambda^l = -\langle \partial \hat{\mathcal{H}}_l / \partial x_\lambda^l \rangle$ being the average force exerted by subsystem l on its surroundings to get the displacements dx_λ^l . Taking expectation value of (2.21) and substituting (2.22) we conclude that the average rate of change of the total thermodynamic entropy is in this case additive, $\langle d\hat{\mathcal{S}}^r \rangle = \sum_l \langle d\hat{\mathcal{S}}_l^r \rangle$, with

$$T_l \langle d\hat{\mathcal{S}}_l^r \rangle = \langle d\hat{\mathcal{H}}_l \rangle - \mu_l \langle d\hat{\mathcal{N}}_l \rangle + \sum_\lambda F_\lambda^l dx_\lambda^l, \quad (2.23)$$

We have arrived in this way to the first law of thermodynamics, through a line of reasoning originally due to Gibbs (1902), generalized here to the quantum case.

Note that for an arbitrary observable \hat{G} , the identity $\langle d\hat{G}/dt \rangle = \partial \langle \hat{G} \rangle / \partial t$ holds whenever the density matrix used to calculate the expectation value satisfies the Liouville-von Neumann equation, as is easily proved by changing to the Heisenberg picture within the expectation value operation, where $d\hat{G}/dt = \partial \hat{G} / \partial t - i[\hat{G}, \hat{H}]$, with \hat{G} depending explicitly on time in the Schrödinger picture via the external parameters, and using the known identity $\text{Tr} \hat{A}[\hat{B}, \hat{C}] = \text{Tr} \hat{C}[\hat{A}, \hat{B}]$. Therefore, *as long as* the local equilibrium density matrix $\hat{\rho}^r$ satisfies the Liouville-von Neumann equation, we can commute the operation $\langle d\hat{G} \rangle = \partial \langle \hat{G} \rangle$ and write (2.23) as the usual form of the first

law of thermodynamics.

The equivalence of (2.23) with the usual form of the first law of thermodynamics

$$T_l \partial_t \langle \hat{\mathcal{S}}_l^r \rangle = \partial_t \langle \hat{\mathcal{H}}_l \rangle - \mu_l \partial_t \langle \hat{\mathcal{N}}_l \rangle + \sum_{\lambda} F_{\lambda}^l \partial_t x_{\lambda}^l, \quad (2.24)$$

then requires that $\hat{\rho}^r$ satisfies the Liouville-von Neumann equation $i \partial_t \hat{\rho}^r = [\hat{H}, \hat{\rho}^r]$, where we use the symbol ∂_t as a shorthand notation for $\partial/\partial t$. For this to be the case, it is necessary from (2.15) that

$$\|\partial_t \hat{\rho}^r\| = O(\Delta), \quad (2.25)$$

since $\hat{\rho}^r$ is expressed in terms of thermodynamic observables. When the thermodynamic limit is taken for each subsystem, we have $\Delta \rightarrow 0$, and then the parameters x_{λ}^l should vary with time so slowly that the state $\hat{\rho}^r$ can be interpreted as “moving” in a locus of equilibrium states, so that $\|\partial_t \hat{\rho}^r\| \rightarrow 0$ in (2.25). These are precisely the *quasistatic* (or reversible) transformations for which the first law involving thermodynamic entropy changes applies, hence the superindex “r” standing for reversible, and the systematic omission of the time subindex in the variables. Note that in this case, the quantity $N_C[\gamma]$ in (2.1) vanishes for any $\gamma = \{x_{\lambda}^l(t), \forall \lambda, l \text{ and } t \in [t_A, t_B]\}$.

A nonzero entropy production appears instead when the subsystems are macroscopic at the atomic scale, but compared to the size of the total system, they are small volume elements, δv_l . In this case, an entropy balance equation may be obtained from (2.24), by using the relations

$$\partial_t \langle \hat{\mathcal{H}}_l \rangle = - \sum_m J_{\mathcal{H}}^{lm} + \sum_{\lambda} \frac{\partial \langle \hat{\mathcal{H}}_l \rangle}{\partial x_{\lambda}^l} \partial_t x_{\lambda}^l, \quad (2.26)$$

$$\partial_t \langle \hat{\mathcal{N}}_l \rangle = - \sum_m J_{\mathcal{N}}^{lm} + \sum_{\lambda} \frac{\partial \langle \hat{\mathcal{N}}_l \rangle}{\partial x_{\lambda}^l} \partial_t x_{\lambda}^l, \quad (2.27)$$

which state that the average macroscopic energy and number of particles of a given subsystem can only change by transport to other subsystems, defining the corresponding currents $J_{\mathcal{H}}^{lm}$ and $J_{\mathcal{N}}^{lm}$ in terms of quantities proportional to the particle velocities, with an appropriate microscopic account for the heat currents, plus terms allowing the technical possibility of a creation or destruction of particles induced by the variation of the external constraints. Substituting these in (2.24) we get

$$\begin{aligned} \partial_t \langle \hat{\mathcal{S}}_l^r \rangle &= \frac{1}{T_l} \sum_{\lambda} \left[\frac{\partial}{\partial x_{\lambda}^l} (\langle \hat{\mathcal{H}}_l \rangle - \mu_l \langle \hat{\mathcal{N}}_l \rangle) + F_{\lambda}^l \right] \partial_t x_{\lambda}^l - \frac{1}{T_l} \sum_m (J_{\mathcal{H}}^{lm} - \mu_l J_{\mathcal{N}}^{lm}) \\ &= \Pi_{\delta v_l} - \Phi_{\delta v_l}, \end{aligned} \quad (2.28)$$

the first term in the first equality being the entropy production term, $\Pi_{\delta v_l}$, and the second one the entropy transport term, $\Phi_{\delta v_l}$. Results consistent with the classical theory are obtained when particle creation or destruction is not observed macroscopically, in which case (2.26) and (2.27) are just the usual conservation laws (continuity equations) and the entropy production in the subsystem reduces to the well-known sum of products of thermodynamic forces times the rate of change of their conjugate external parameters

$$\Pi_{\delta v_l} = \frac{1}{T_l} \sum_{\lambda} F_{\lambda}^l \partial_t x_{\lambda}^l, \quad (\text{classical}). \quad (2.29)$$

The presentation given here can be straightforwardly generalized by considering local equilibrium Gibbs ensembles more general than (2.8), that is, by augmenting the thermodynamic entropy operator (2.20) with terms proportional to the components of the macroscopic linear and angular momentum operators of each subsystem [Landau and Lifshitz \(1980\)](#), with (2.26) and (2.27) expanded to include the conservation laws of their respective expectation values.

Note that we have kept the superindex “r” (although not strictly with its original connotation) in (2.28) because, even though the thermodynamic limit is not taken for each subsystem, which would make $\Delta \rightarrow 0$ and the processes necessarily quasistatic,

the fact that the volume elements, δv_l , are macroscopic at the atomic scale still implies that Δ is very small and hence, from (2.25), that the variations $\partial_t \hat{\rho}^r$ should correspondingly be very small in the norm. As mentioned in section 2.3, we then see why the classical theory works well for *slow* processes, i.e. those for which the time to get relaxation to equilibrium within each volume element is much shorter than the time to get equilibrium among them.

The discussion in this section elucidates the problems with the local equilibrium assumption and previous theories of entropy production, which rely on expressions of the type (2.24) together with conservation laws, like (2.26) and (2.27), as in the classical theory. As we have made explicit, developing a theory of entropy production from (2.24) inherently assumes that the correlations among the subsystems of a large isolated system are negligible *for all times*, and using (2.26) in this theory takes for granted that an appropriate mechanical description of the microscopics of heat currents have been univocally achieved.

We now propose a way to derive an entropy balance equation for the subsystems of a general isolated system from first principles, starting from the Liouville-von Neumann equation for the density matrix of the isolated system, which does not rely on the above assumptions.

2.5 Master equation for the thermodynamic entropy operator

We generalize the thermodynamic description to include subsystems which are not distinguished by spatial boundaries and which are not necessarily macroscopic at the atomic scale. The key point to borrow from thermodynamics is the existence of the *thermodynamic basis* $\{|\boldsymbol{\alpha}\rangle\}$ and the interpretation of thermodynamic observables

as those which are diagonal in this basis. That is, we consider an isolated quantum system (containing possible reservoirs) which has a Hamiltonian $\hat{\mathcal{H}}$ representing the energy of uncoupled subsystems, as before, and study the dynamics when the perturbation, \hat{V} , mixing the degrees of freedom of the different subsystems, or a set of them, is turned on.

The Hamiltonian of the total system is then given by $\hat{H} = \hat{\mathcal{H}} + \hat{V}$, and the situations of interest include phenomena such as quantum quenches [Polkovnikov et al. \(2011\)](#); [Yukalov \(2011\)](#); [D'Alessio et al. \(2016\)](#); [Gogolin and Eisert \(2016\)](#); [Eisert et al. \(2015\)](#) or the response to applied fields [Kubo \(1957\)](#); [Suzuki \(2011, 2012\)](#). After preparation of the system in an initial statistical state of the form

$$\hat{\rho}_0 = \exp(-\hat{S}_0), \quad (2.30)$$

with \hat{S}_0 an arbitrary (in general unbounded) hermitian operator with $[\hat{S}_0, \hat{V}] \neq 0$, the nonequilibrium state is described by the evolved density matrix $\hat{\rho}_t$, and we define the entropy operator \hat{S}_t by

$$\hat{\rho}_t = \exp(-\hat{S}_t), \quad \text{or} \quad \hat{S}_t = -\ln \hat{\rho}_t, \quad (2.31)$$

which can always be written since the density matrix is positive-definite. This exponential representation of the density matrix is not new; it is a generalized form [Suzuki \(1998, 2012\)](#) of the nonequilibrium statistical operator introduced by [Zubarev, Zubarev \(1994\)](#); [Zubarev and Kalashnikov \(1971\)](#) and obtained for the case of steady states by [Hershfield \(1993\)](#).

As discussed in the previous section, our *new* thermodynamic entropy operator, $\hat{\mathcal{S}}_t = -\mathcal{D} \ln \hat{\rho}_t$, is obtained from \hat{S}_t by projecting to the space of operators diagonal in the basis $\{|\alpha\rangle\}$ of eigenstates of $\hat{\mathcal{H}}$. We now establish the second law of thermodynamics for nonequilibrium transformations of the total system. For this, we consider for

simplicity the specific situation of initial states diagonal in the thermodynamic basis, e.g. those of local equilibrium form as in (2.8), for which $\hat{S}_0^\sim = 0$ or $\hat{S}_0 = \hat{S}_0$. These initial states are usually assumed in practice Mori (1958); Kubo (1957); Hershfield (1993), e.g. in transport problems.

Let us denote the diagonal (or thermodynamic) part of the density matrix of the system as

$$\hat{\varrho}_t = \mathcal{D}\hat{\rho}_t. \quad (2.32)$$

The occupation probability of the state $|\alpha\rangle$ is obtained by taking matrix elements $P_{\alpha;t} = \langle\alpha|\hat{\varrho}_t|\alpha\rangle$. The proof now follows in steps by first using a corollary to Klein's inequality Wehrl (1978) which states that for any *concave* function $f(x)$ we have

$$\text{Tr } f(\hat{\varrho}_t) \geq \text{Tr } f(\hat{\rho}_t). \quad (2.33)$$

By choosing the concave function $f(x) = -x \ln(x)$, we easily get

$$-\text{Tr } \hat{\varrho}_t \ln(\hat{\varrho}_t) \geq -\text{Tr } \hat{\rho}_t \ln \hat{\rho}_t \quad \text{or} \quad S_{d;t} \geq S_{vN;t}, \quad (2.34)$$

where we have denoted $S_{d;t} = -\sum_{\alpha} P_{\alpha;t} \ln P_{\alpha;t}$ as the diagonal entropy Polkovnikov et al. (2011); Polkovnikov (2011); Santos et al. (2011); Levi et al. (2016) and $S_{vN;t}$ is the well-known von Neumann entropy. Using the time-invariance of $S_{vN;t}$ under the unitary evolution of the isolated system together with the fact that the initial state is diagonal, so that $S_{d;0} = S_{vN;0}$, then (2.34) implies Polkovnikov et al. (2011); Polkovnikov (2011)

$$S_{d;t} \geq S_{d;0}. \quad (2.35)$$

We use this result and the Husimi-Mori lemma Husimi (1940); Mori (1956) which

states that for any *convex* function $g(x)$ and state $|\psi\rangle$ we have

$$\langle\psi|g(\hat{\rho}_t)|\psi\rangle \geq g(\langle\psi|\hat{\rho}_t|\psi\rangle), \quad (2.36)$$

to show that, if we choose the convex function $g(x) = -\ln(x)$ so that $-\langle\boldsymbol{\alpha}|\ln \hat{\rho}_t|\boldsymbol{\alpha}\rangle \geq -\ln P_{\boldsymbol{\alpha};t}$, the thermodynamic entropy satisfies

$$\mathcal{S}_t = \langle\hat{\mathcal{S}}_t\rangle = -\sum_{\boldsymbol{\alpha}} P_{\boldsymbol{\alpha};t} \langle\boldsymbol{\alpha}|\ln \hat{\rho}_t|\boldsymbol{\alpha}\rangle \geq S_{d;t} \geq \mathcal{S}_0, \quad (2.37)$$

where $\mathcal{S}_0 = S_{d;0} = S_{vN;0}$ by the assumption of the initial diagonal state. For our isolated system for which there is no entropy to be transported outside of its boundaries, this proves that \mathcal{S}_t satisfies the second law of thermodynamics.

Note that, by splitting $\hat{\rho}_t = \hat{\varrho}_t + \hat{\rho}_t^\sim$ and using the convenient resolvent representation of the logarithm of an operator sum [Suzuki \(1998\)](#)

$$\ln(\hat{A} + \hat{B}) = \int_0^\infty dx \left(\frac{1}{x+1} - \frac{1}{x+\hat{A}+\hat{B}} \right), \quad (2.38)$$

we can expand the thermodynamic entropy as

$$\begin{aligned} \mathcal{S}_t = S_{d;t} + \sum_{\boldsymbol{\alpha}, \boldsymbol{\beta}(\neq \boldsymbol{\alpha})} \left[\frac{1}{(P_{\boldsymbol{\beta};t} - P_{\boldsymbol{\alpha};t})} - \frac{P_{\boldsymbol{\alpha};t}}{(P_{\boldsymbol{\beta};t} - P_{\boldsymbol{\alpha};t})^2} \ln \frac{P_{\boldsymbol{\beta};t}}{P_{\boldsymbol{\alpha};t}} \right] |\langle\boldsymbol{\alpha}|\hat{\rho}_t^\sim|\boldsymbol{\beta}\rangle|^2 \\ + O(\langle|\hat{\rho}_t^\sim|^3\rangle), \end{aligned} \quad (2.39)$$

with $\mathcal{S}_t - S_{d;t} \geq 0$ due to (2.37); therefore the thermodynamic entropy, unlike the diagonal entropy, is able to capture entropy increasing processes due to quantum correlations or entanglement among the different subsystems, that are encapsulated in the off-diagonal elements of the density matrix. When these quantum correlations are negligible which, as discussed in section 2.4, is the case when each subsystem is macroscopic, the diagonal entropy *becomes* the thermodynamic entropy according

to (2.39), and due to the quasistatic (or slow) nature of the global transformations involved in this case, the thermodynamic basis may be referred to as the adiabatic basis Polkovnikov (2008); Polkovnikov et al. (2011).

The thermodynamic entropy, unlike the diagonal and von-Neumann entropies, satisfies the third law of thermodynamics in a transparent way. The third law states that the thermodynamic entropy at zero temperature must be zero. The standard argument is that at zero temperature any physical state is *pure*. For an arbitrary pure state $|\psi\rangle$, there is always an orthonormal basis of Hilbert space which has this state as one of its elements (construct it via the Gram-Schmidt procedure starting from $|\psi\rangle$). Denote this basis, $\{|\psi_r\rangle\}$, and order its elements such that $|\psi\rangle = |\psi_1\rangle$.

We take the above basis as the reference for “diagonal” in the following calculation of the thermodynamic entropy of pure states, which is justified because von Neumann (1943) has shown that *any* pure state can be converted *reversibly and adiabatically* to any other pure state, so calculating the thermodynamic entropy of $|\psi_r\rangle$ is equivalent to calculating the thermodynamic entropy of a given $|\alpha\rangle$. Indeed, the reader may use $|\psi_r\rangle = |\alpha\rangle$ in the following argument without loss of generality.

With this in mind, we then have for the diagonal and von-Neumann entropies

$$\begin{aligned} S_d(\psi) &= S_{vN}(\psi) = - \sum_r P_r \ln P_r, \\ &= -1 \cdot \ln(1) - \sum_{r \neq 1} 0 \cdot \ln(0), \end{aligned} \tag{2.40}$$

where P_r is the probability that the system be found in state $|\psi_r\rangle$. Eq. (2.40) is usually *understood* to be zero Wehrl (1978), although it is clearly an undetermined quantity—if no limiting procedure is invoked—since, taken at face value, $-0 \cdot \ln(0) = 0 \cdot \infty$.

The thermodynamic entropy of pure states is well-defined and readily vanishes. In order to show this, we denote the density matrices (projectors) $\hat{\rho}_r = |\psi_r\rangle\langle\psi_r|$, with

$\sum_r \hat{\rho}_r = \hat{1}$. We can then write

$$\ln \hat{\rho}_1 = \ln(\hat{1} - \sum_{r \neq 1} \hat{\rho}_r) = - \sum_{u=1}^{\infty} (\sum_{r \neq 1} \hat{\rho}_r)^u / u, \quad (2.41)$$

the last expansion using the operator equivalent of $\ln(1 - x) = - \sum_{u=1}^{\infty} x^u / u$ valid for $|x| < 1$. The operator equivalent of this last inequality is obtained by considering the norm $\|\hat{A}\| = \sqrt{\text{Tr}(\hat{A}^\dagger \hat{A})}$ and noticing that, by taking the trace with respect to an orthonormal basis, $\|\sum_r \hat{\rho}_r\| = \|\hat{1}\| = 1$ so removing $\hat{\rho}_1$ from the sum to get $\sum_{r \neq 1} \hat{\rho}_r$ decreases the norm, since $\hat{\rho}_1$ is a projection operator and then positive definite.

Using this, we can compute the thermodynamic entropy of the state $|\psi\rangle$ as

$$\mathcal{S}(\psi) = - \sum_r \langle \psi_r | \hat{\rho}_1 \mathcal{D} \ln(\hat{\rho}_1) | \psi_r \rangle = - \langle \psi | \ln(\hat{\rho}_1) | \psi \rangle, \quad (2.42)$$

which vanishes exactly since $|\psi\rangle = |\psi_1\rangle$ is orthogonal to all $|\psi_{r \neq 1}\rangle$ involved in the last equality of (2.41). This establishes the third law of thermodynamics.

We are after an entropy balance equation for the subsystems, so we need an equation of motion for $\hat{\mathcal{S}}_t$ and a procedure to get from this one for each subsystems, as in the previous section. This can be obtained by first noting that the usual unitary evolution of the density matrix implies that \hat{S}_t also satisfies the Liouville-von Neumann equation [Suzuki \(1998\)](#) satisfied by $\hat{\rho}_t$. We have

$$i \partial_t \hat{S}_t = [\hat{H}, \hat{S}_t] \equiv L \hat{S}_t. \quad (2.43)$$

This allows us to follow exactly the same procedure originally used with the density matrix [Nakajima \(1958\)](#); [Zwanzig \(1960\)](#) to derive an equation of motion for its diagonal part, $\hat{\rho}_t$, the so-called Nakajima-Zwanzig generalized master equation. That is, we split the entropy operator into a diagonal and nondiagonal part, with respect to the eigenbasis of $\hat{\mathcal{H}}$, as $\hat{S}_t = \hat{\mathcal{S}}_t + \hat{S}_t^\sim$, and obtain an equation of motion for the

diagonal part using Zwanzig's integral [Zwanzig \(1960\)](#)

$$i\partial_t \hat{\mathcal{S}}_t = \mathcal{D}L \hat{\mathcal{S}}_t + \mathcal{D}L e^{-it\mathcal{N}L} \hat{\mathcal{S}}_0^\sim - i \int_0^t d\tau K_\tau \hat{\mathcal{S}}_{t-\tau}, \quad (2.44)$$

where the memory kernel is defined as [Zwanzig \(1964\)](#)

$$K_\tau = \mathcal{D}L e^{-i\tau\mathcal{N}L} \mathcal{N}L. \quad (2.45)$$

Eq (2.44) displays the memory expected for the rate of change of the thermodynamic entropy on its previous values, a feature not incorporated in other formulations such as the one given by [Robertson \(1966\)](#).

Now, it is easy to verify that $\mathcal{D}L\mathcal{D} = 0$ for any Hamiltonian, [Zwanzig \(1964\)](#) therefore the first term in (2.44) vanishes and, with our initial diagonal states implying $\hat{\mathcal{S}}_0^\sim = 0$, we are left with the integro-differential equation

$$\partial_t \hat{\mathcal{S}}_t = - \int_0^t d\tau K_\tau \hat{\mathcal{S}}_{t-\tau}. \quad (2.46)$$

Although an exact solution for (2.46), as well as for the similar equation satisfied by $\hat{\partial}_t$, can easily be found by a Laplace transformation followed by an inversion

$$\hat{\mathcal{S}}_t = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} ds \frac{e^{st}}{s + K_s} \hat{\mathcal{S}}_0, \quad \text{with } c > 0, \quad (2.47)$$

where K_s is the Laplace transform of the memory kernel, obtained from (2.45) as

$$K_s = \mathcal{D}L \frac{1}{s + i\mathcal{N}L} \mathcal{N}L, \quad (2.48)$$

we restrict here, for the sake of a clear presentation and for comparison with the classical results, to the Born-Markov approximation for *weakly* coupled subsystems, leaving a more general discussion for another publication. This approximation, which

is justified in the limit of very weak coupling potentials, \hat{V} , and very long times (Van Hove limit [Van Hove \(1955b\)](#); [Davies \(1974\)](#)) amounts to neglecting memory effects in (2.46). In practice, this works for times *after* any transient effect or prethermalization plateau [Stark and Kollar](#); [Bertini et al. \(2015\)](#); [Nessi and Iucci](#) of the isolated system has passed. We then have in this limit

$$\partial_t \hat{\mathcal{S}}_t = - \lim_{s \rightarrow 0^+} K_s \hat{\mathcal{S}}_t, \quad (2.49)$$

where K_s and $\hat{\mathcal{S}}_t$, after being expanded in powers of \hat{V} , are truncated up to the lowest orders, for which the well-known identity for the resolvent operator expansion

$$(A + B)^{-1} = A^{-1} - A^{-1}B(A + B)^{-1}, \quad (2.50)$$

is very useful. Taking expectation value of (2.49), and noting that for a diagonal operator \hat{A} we have $\langle \hat{A} \rangle_t = \text{Tr}(\hat{\rho}_t \hat{A}) = \text{Tr}(\hat{\varrho}_t \hat{A})$, the average rate of change of the thermodynamic entropy in the Born-Markov limit is then

$$\langle \partial_t \hat{\mathcal{S}}_t \rangle = \sum_{\alpha\alpha'} P_\alpha W_{\alpha\alpha'} \ln \frac{P_\alpha}{P_{\alpha'}}. \quad (2.51)$$

with the transition rates $W_{\alpha\alpha'} = 2\pi\delta(\varepsilon_\alpha - \varepsilon_{\alpha'})|V_{\alpha\alpha'}|^2$, calculated in the lowest order in the coupling potential using Fermi's golden rule. Here, we have derived the transition rates from (2.48) and (2.49), by using the representation of the delta function [Lippmann and Schwinger \(1950\)](#)

$$\lim_{s \rightarrow 0^+} \text{Re} \frac{1}{s + i\omega} = \pi\delta(\omega). \quad (2.52)$$

Moreover, $P_\alpha = \langle \alpha | \hat{\varrho}_t^{(0)} | \alpha \rangle$ is the occupation probability of the state $|\alpha\rangle$ in its lowest-order approximation [Nakajima \(1958\)](#), which also satisfies the Born-Markov limit of

the generalized master equation, that is, the transport (or Pauli) equation

$$\partial_t P_\alpha = \sum_{\alpha'} (P_{\alpha'} W_{\alpha'\alpha} - P_\alpha W_{\alpha\alpha'}). \quad (2.53)$$

The right hand side of (2.51) can be rearranged to yield the quantum version, in the Born-Markov limit, of the entropy balance equation. We find

$$\langle \partial_t \hat{\mathcal{S}}_t \rangle = \Pi - \Phi, \quad (2.54)$$

where the average rate of entropy produced in the system is interpreted as [Schnakenberg \(1976\)](#); [Luo et al. \(1984\)](#); [Seifert \(2005\)](#); [Esposito and Van den Broeck \(2010\)](#); [Tomé and de Oliveira \(2012\)](#)

$$\Pi = \frac{1}{2} \sum_{\alpha, \alpha'} (P_\alpha W_{\alpha\alpha'} - P_{\alpha'} W_{\alpha'\alpha}) \ln \frac{P_\alpha W_{\alpha\alpha'}}{P_{\alpha'} W_{\alpha'\alpha}}, \quad (2.55)$$

and the average entropy flux to the surroundings as

$$\Phi = \frac{1}{2} \sum_{\alpha, \alpha'} (P_\alpha W_{\alpha\alpha'} - P_{\alpha'} W_{\alpha'\alpha}) \ln \frac{W_{\alpha\alpha'}}{W_{\alpha'\alpha}}. \quad (2.56)$$

Of course, the latter must be zero for an isolated system since a global entropy current finds nowhere to go in this case. The vanishing of this quantity is clearly seen from the symmetry of the transition rates $W_{\alpha\alpha'}$ under the interchange of indices, resulting from the hermiticity of the perturbation \hat{V} . A nonvanishing entropy current is obtained however when we consider the local entropy production in a subsystem of a larger system, as in the electrical conduction problem of section 2.7.

Note that Π is a sum of terms of the form $(x-y) \ln(x/y)$ so is always *non-negative*. It vanishes for reversible transformations (local equilibrium) or in equilibrium due to detailed balance, $P_\alpha^r W_{\alpha\alpha'} = P_{\alpha'}^r W_{\alpha'\alpha}$, this being a statistical statement of the second

law of thermodynamics in the Clausius form. The outlined method is the one that we shall follow in section 2.7 for the electrical conduction problem to derive an entropy balance equation for the electronic subsystem in the Born-Markov limit, based on the transport equation for the total electrons + phonons + field system, without any need to invoke expressions like (2.24) together with extra conservation laws.

One of the advantages of our approach, besides being grounded on fundamental facts regarding the nature of thermodynamic observables is that, as opposed to actively studied relative-entropy formulations Spohn (1978); Spohn and Lebowitz (1978); Esposito et al. (2010) of quantum entropy production, it can be generalized to initial states with correlations among the subsystems, i.e. not of the local equilibrium form. This is very important since the neglect of correlations in the state of an isolated system is inconsistent with the specification of its energy Philippot (1961).

We have safely ignored this fact in our present discussion because the consideration of a nonvanishing second term in (2.44), due to $\hat{S}_0^\sim \neq 0$, only adds the term

$$\frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} ds \frac{e^{st}}{s + K_s} \mathcal{D}L \frac{1}{s + i\mathcal{N}L} \hat{S}_0^\sim, \quad (2.57)$$

to the solution (2.47). However, it is easily seen that expressions containing \hat{S}_0^\sim contribute higher order terms in the weak coupling expansion embodied in the Born-Markov limit and then are negligible; the same happens Nakajima (1958) for the contributions coming from $\hat{\rho}_0^\sim$ in the Born-Markov limit of the generalized master equation for $\hat{\rho}_t$. Therefore, our formalism has room to study memory effects and strong correlations in the initial state by only straightforward modifications. These memory effects are the ones responsible for heat transport depending on the path of thermodynamic states in phenomenological thermodynamics.

2.6 Relation with classical stochastic thermodynamics

We now show that our result, (2.51), is consistent with the result for the average rate of change of the thermodynamic entropy obtained in Onsager's classical theory. We consider an isolated macroscopic system which has been left alone for a very long time (aged system). The classical thermodynamic state is described by a set of extensive variables, such as energy, mass, electric charge, etc., which randomly fluctuate about their equilibrium values and whose values define the classical state of the system. This state is represented by the symbol \mathbf{a}_t (shifted to vanish in equilibrium), whose successive values in time describe a stationary stochastic process.

It can be shown that, if the fluctuations follow a Gaussian process, which can be argued to be the case if the extensive variables are algebraic sums of very many independent (weakly coupled) "microscopic" quantities so that the central limit theorem can be invoked and, if in addition the process is Markovian, then the joint probability distribution,

$$\Omega(\mathbf{a}', \Delta t, \mathbf{a}'') = P_{\mathbf{a}'} P_{\mathbf{a}'\mathbf{a}''}(\Delta t), \quad (2.58)$$

for observing the values $\mathbf{a}_{t'} = \mathbf{a}'$ and $\mathbf{a}_{t''} = \mathbf{a}''$ at the respective times separated by an interval $\Delta t = t'' - t'$, with $P_{\mathbf{a}'\mathbf{a}''}(\Delta t)$ the corresponding conditional probability to make a transition between these states, is given by Onsager's principle [Onsager \(1931\)](#); [Hashitsume \(1952\)](#); [Onsager and Machlup \(1953\)](#) which we write as ¹

$$2 \ln \Omega(\mathbf{a}', \Delta t, \mathbf{a}'') = \mathcal{S}_{\mathbf{a}'} + \mathcal{S}_{\mathbf{a}''} + \left(\int_{t'}^{t''} d\tau \dot{\mathcal{S}} \right)_{\min}, \quad (2.59)$$

¹ We are interpreting the normal forward evolution as the mirror image in time of that originally considered by Onsager and Machlup since, as pointed out by them, the mirror image is the only one that satisfies the initial conditions nontrivially.

where the path of integration is the trajectory, \mathbf{a}_τ , which makes the integral a minimum, subject to the conditions $\mathbf{a}_{t'} = \mathbf{a}'$ and $\mathbf{a}_{t''} = \mathbf{a}''$. Clearly, if we take the limit $\Delta t \rightarrow 0$, the integral tends to $\dot{\mathcal{S}}_{\mathbf{a}'}\Delta t$, where $\dot{\mathcal{S}}_{\mathbf{a}'}$ is the entropy production rate in the state \mathbf{a}' , whose entropy is related to the probability distribution, $P_{\mathbf{a}'}$, by Boltzmann's principle. Subtracting the time-reversed expression of Onsager's principle from (2.59) we get, in the limit $\Delta t \rightarrow 0$, the alternative form

$$\ln \frac{\Omega(\mathbf{a}', \Delta t, \mathbf{a}'')}{\Omega(\mathbf{a}'', -\Delta t, \mathbf{a}')} = \frac{1}{2}(\dot{\mathcal{S}}_{\mathbf{a}'} + \dot{\mathcal{S}}_{\mathbf{a}''})\Delta t, \quad (2.60)$$

We now average (2.60) over the joint distribution (2.58), which is expanded up to linear order in Δt by writing the transition probabilities to go from \mathbf{a}' to \mathbf{a}'' after a time Δt as

$$P_{\mathbf{a}'\mathbf{a}''}(\Delta t) = \delta_{\mathbf{a}'\mathbf{a}''} + W_{\mathbf{a}'\mathbf{a}''}\Delta t = P_{\mathbf{a}''\mathbf{a}'}(-\Delta t), \quad (2.61)$$

the last equality being the statement of Onsager's microscopic reversibility [Onsager \(1931\)](#); [Casimir \(1945\)](#) and leading to the symmetry of the transition rates, $W_{\mathbf{a}'\mathbf{a}''}$, under the interchange of indices. This symmetry allows to write the averaged left-hand side of (2.60) as $\Delta t \sum_{\mathbf{a}'\mathbf{a}''} P_{\mathbf{a}'} W_{\mathbf{a}'\mathbf{a}''} \ln(P_{\mathbf{a}'}/P_{\mathbf{a}''})$ and the right-hand side as $\Delta t \sum_{\mathbf{a}'} P_{\mathbf{a}'} \dot{\mathcal{S}}_{\mathbf{a}'}$. Therefore, by recognizing the latter sum as $\langle \dot{\mathcal{S}} \rangle$, we get the expression

$$\langle \dot{\mathcal{S}} \rangle = \sum_{\mathbf{a}'\mathbf{a}''} P_{\mathbf{a}'} W_{\mathbf{a}'\mathbf{a}''} \ln \frac{P_{\mathbf{a}'}}{P_{\mathbf{a}''}}, \quad (2.62)$$

which gives the desired link with our theory, by comparing with (2.51). We remark that (2.60) is of the same form [Bustamante et al. \(2005\)](#)

$$\ln \frac{P_{\Delta t}(\sigma)}{P_{\Delta t}(-\sigma)} = \sigma \Delta t \quad (2.63)$$

as Gallavotti and Cohen fluctuation theorem [Gallavotti and Cohen \(1995\)](#) if we read $(1/2)(\dot{\mathcal{S}}_{\mathbf{a}'} + \dot{\mathcal{S}}_{\mathbf{a}''})$, as a realization of the random number $\sigma = (1/2)(\dot{\mathcal{S}}_{\mathbf{a}_{t'}} + \dot{\mathcal{S}}_{\mathbf{a}_{t''}})$,

representing the average entropy production in going from $\mathbf{a}_{t'}$ to $\mathbf{a}_{t''}$ during a time interval Δt along the stochastic trajectory of states; and translate the joint probability, $\Omega(\mathbf{a}', \pm\Delta t, \mathbf{a}'')$, to have the state realizations $\mathbf{a}_{t'} = \mathbf{a}'$ and $\mathbf{a}_{t''} = \mathbf{a}''$, in a forward ($+\Delta t$) or backward ($-\Delta t$) evolution, to the corresponding probabilities $P_{\Delta t}(\pm\sigma)$ to have the realization, $(1/2)(\dot{\mathcal{S}}_{\mathbf{a}'} + \dot{\mathcal{S}}_{\mathbf{a}''})$, of σ or its time-reversed value.

2.7 Entropy production in electrical conduction

We next apply the formalism to a model of independent electrons coupled to phonons in the presence of an electric field. We are interested in the average rate of entropy produced in the electronic system and transported to the phonons in the steady state. The picture is then that of a large system divided into three subsystems, the electrons, the phonons, and the sources of the field. In the thermodynamic description we parametrize, as usual, the coupling to the latter by introducing \mathbf{E}_t and forgetting about the structure of this subsystem.

The Hamiltonian of the total system is then

$$\hat{H} = \hat{H}_{\text{el}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{el-ph}} + \hat{H}_{F;t}, \quad (2.64)$$

where $\hat{H}_{\text{el}} = \sum_k \epsilon_k \hat{c}_k^\dagger \hat{c}_k$ is the kinetic energy operator for the electrons, which are assumed to be free except for their interaction with the field and the phonons, the energy operator of the phonon subsystem is $\hat{H}_{\text{ph}} = \sum_q \omega_q \hat{a}_q^\dagger \hat{a}_q$, and the electron-phonon interaction is bilinear in electron operators and linear in phonon operators

$$\hat{H}_{\text{el-ph}} = \sum_{qkk'} M_{k'k}^q \hat{c}_{k'}^\dagger \hat{c}_k (\hat{a}_q + \hat{a}_{-q}^\dagger), \quad (2.65)$$

with $M_{k'k}^q$ representing the strength of the coupling. The generalization to multiple

electronic bands and multiple phonon branches is straightforward and does not change the results. Finally, $\hat{H}_{F;t}$ represents the effects of the applied electric field, \mathbf{E}_t , and can be written in first-quantized notation as $\hat{H}_{F;t} = -e \mathbf{E}_t \cdot \sum_e \hat{\mathbf{x}}_e$, where $\hat{\mathbf{x}}_e$ is the displacement of electron e from some arbitrarily chosen reference position.

Up to time $t = 0$ we have a collection of electrons in local equilibrium with the lattice vibrations of a metal at a temperature T , and no applied electric field, i.e. $\mathbf{E}_0 = 0$. The initial state is then of the form

$$\hat{\rho}_0 = Z^{-1} \exp[-(\hat{\mathcal{H}}_0 - \mu \hat{\mathcal{N}}_{\text{el}})/T], \quad (2.66)$$

where $Z = Z_{\text{el}} Z_{\text{ph}}$ is the grand partition function, $\hat{\mathcal{N}}_{\text{el}}$ is the operator for the total number of electrons, and $\hat{\mathcal{H}}_0$ is the Hamiltonian of the uncoupled subsystems

$$\hat{\mathcal{H}}_0 = \hat{H}_{\text{el}} + \hat{H}_{\text{ph}}, \quad (2.67)$$

whose eigenstates, constituting the thermodynamic basis, are

$$|\boldsymbol{\alpha}\rangle = |n_1 n_2 \cdots n_k \cdots\rangle |N_1 N_2 \cdots N_q \cdots\rangle = |n; N\rangle, \quad (2.68)$$

which represent the number of electrons, $\{n_k\}$, and phonons, $\{N_q\}$, in each single-particle state.

The electric field is turned on at time $t = 0^+$ to a constant value, i.e. $\mathbf{E}_t = \mathbf{E}$ for $t > 0$, and the subsystems are subsequently coupled. In the notation of section 2.5 we then have in the generalized thermodynamic description

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{H}_F, \quad \hat{V} = \hat{H}_{\text{el-ph}}. \quad (2.69)$$

Note that \hat{V} is the coupling which fully mixes the degrees of freedom of the different subsystems (like the \hat{H}_{lm} in section 2.4), which need not be separated by spatial

boundaries. We now explain with some detail how the perturbation scheme developed in section 2.5 applies to the present case. However, we only need to concentrate on how the transport equation is obtained in the Born-Markov limit, since this suffices to get the average rate of entropy production.

The idea is then to first derive the transport equation for the total system from the Liouville-von Neumann equation; we do it much in the same spirit as [Kohn and Luttinger \(1957\)](#) did for elastic electronic scattering and generalized by [Argyres \(1961\)](#) to inelastic scattering. Having this transport equation, the average rate of change of the total thermodynamic entropy in the Born-Markov limit is

$$\langle \partial_t \hat{\mathcal{S}}_t \rangle = - \sum_{\alpha} (\partial_t P_{\alpha}) \ln P_{\alpha}, \quad (2.70)$$

as can easily be verified by using (2.53) in (2.51). By proceeding with the transport or quantum Boltzmann equation for the electronic subsystem, we obtain a simple expression for the electronic entropy production.

For the purpose of the present discussion, it suffices to work with the Liouville-von Neumann equation to first order in the electric field. That is, with $\hat{\rho}_t = \hat{\rho}_0 + \hat{\rho}_{1;t}$ and $\hat{\rho}_{1;t}$ linear in the electric field, we write

$$i\partial_t \hat{\rho}_{1;t} = [\hat{\mathcal{H}}_0 + \hat{V}, \hat{\rho}_{1;t}] + [\hat{H}_F, \hat{\rho}_0], \quad (2.71)$$

where $\hat{\rho}_{1;0} = 0$. The Laplace transform of this equation, with $\hat{\rho}_{1;s} = \int_0^{\infty} e^{-st} \hat{\rho}_{1;t}$, reads

$$is\hat{\rho}_{1;s} = (\mathcal{L}_0 + L_V)\hat{\rho}_{1;s} + s^{-1}L_F\hat{\rho}_0. \quad (2.72)$$

With $\hat{\rho}_{1;s} = \mathcal{D}\hat{\rho}_{1;s}$ and $\hat{\rho}_{1;s}^{\sim} = \mathcal{N}\hat{\rho}_{1;s}$, we separate this equation into a diagonal and a

non-diagonal part, obtaining, respectively, the coupled algebraic equations

$$is\hat{\varrho}_{1;s} = \mathcal{D}L_V \hat{\rho}_{1;s}^{\sim} + s^{-1}\mathcal{D}L_F\hat{\rho}_0, \quad (2.73)$$

$$[is + \mathcal{N}(\mathcal{L}_0 + L_V)]\hat{\rho}_{1;s}^{\sim} = \mathcal{N}L_V \hat{\varrho}_{1;s} + s^{-1}\mathcal{N}L_F\hat{\rho}_0. \quad (2.74)$$

Solving for $\hat{\rho}_{1;s}^{\sim}$ in (2.74) and substituting the result in (2.73) we get a decoupled equation for $\hat{\varrho}_{1;s}$, which in the lowest Born approximation for the electron-phonon scattering reads

$$is\hat{\varrho}_{1;s} = \mathcal{D}L_V \frac{1}{is + \mathcal{N}\mathcal{L}_0} \mathcal{N}L_V \hat{\varrho}_{1;s} + s^{-1}\mathcal{D}L_F\hat{\rho}_0. \quad (2.75)$$

From this, the transport equation for the total system easily arises in the Born-Markov limit by taking the Laplace inverse and neglecting memory terms. In terms of the occupation probabilities $P_{\alpha} = \langle \alpha | \hat{\varrho}_t | \alpha \rangle$ we get

$$\partial_t P_{\alpha} = \frac{1}{i} (L_F \hat{\rho}_0)_{\alpha} + \sum_{\alpha'} (P_{\alpha'} W_{\alpha'\alpha} - P_{\alpha} W_{\alpha\alpha'}) \quad (2.76)$$

with the transition rates induced by the electron-phonon coupling $W_{\alpha\alpha'} = 2\pi\delta(\varepsilon_{\alpha} - \varepsilon_{\alpha'}) |\langle \alpha | \hat{H}_{\text{el-ph}} | \alpha' \rangle|^2$. We have then derived the transport equation for the total system, in terms of which the average rate of change of the total thermodynamic entropy can be calculated, in the Born-Markov limit, using (2.70).

To proceed with the calculation of the entropy production of the electronic subsystem, we note that

$$P_{\alpha} = P_n^{\text{el}} P_N^{\text{ph}} \chi_{nN}^{\text{el-ph}}, \quad (2.77)$$

where P_n^{el} is the probability that the electrons are in the Fock state $|n\rangle$ regardless of the state of the phonons, P_N^{ph} is the probability that the phonons are in the Fock state $|N\rangle$ regardless of the state of the electrons, and $\chi_{nN}^{\text{el-ph}}$ is the conditional probability that the total system is in the state $|\alpha\rangle$ in (2.68), given that the electron and phonon

subsystems are in states $|n\rangle$ and $|N\rangle$, respectively, without “knowing” about each other. Clearly, $\chi_{nN}^{\text{el-ph}}$ is a function of the electron-phonon coupling strength, and can then be expanded in a power series of it

$$\chi_{nN}^{\text{el-ph}} = 1 + \chi_{nN}^{\text{el-ph}(1)} + \chi_{nN}^{\text{el-ph}(2)} + \dots . \quad (2.78)$$

In the lowest Born approximation for the electron-phonon scattering, the electron and phonon subsystems are uncorrelated, i.e. $\chi_{nN}^{\text{el-ph}} = 1$, which is the usual Born-Oppenheimer approximation, and then by substituting (2.76) and (2.77) into (2.70), the average rate of change of the thermodynamic entropy of the total system turns out to be additive. For the electronic subsystem we have

$$\langle \partial_t \hat{\mathcal{S}}_t \rangle_{\text{el}} = - \sum_n (\partial_t P_n^{\text{el}}) \ln P_n^{\text{el}}, \quad (2.79)$$

where the normalization condition $\sum_N P_N^{\text{ph}} = 1$ has been used. Here, the transport equation for the electronic subsystem is obtained from (2.76) by summing over N

$$\partial_t P_n^{\text{el}} = \frac{1}{i} \sum_N (L_F \hat{\rho}_0)_{nN, nN} + \sum_{n'} (P_{n'}^{\text{el}} \Gamma_{n'n} - P_n^{\text{el}} \Gamma_{nn'}), \quad (2.80)$$

where we have defined the phonon-averaged reduced transition rates $\Gamma_{nn'}$ as

$$\Gamma_{nn'} = \sum_N P_N^{\text{ph}} \sum_{N'} W_{nN, n'N'}. \quad (2.81)$$

We can still go further and use the assumed statistical independence of the electrons to factorize their probability distribution into the probabilities of the one-electron states

$$P_n^{\text{el}} = p_{n_1} p_{n_2} \cdots p_{n_k} \cdots, \quad (2.82)$$

where p_{n_k} is the probability that the one-electron state with quantum number k has

occupation $n_k = 0, 1$. Substituting this in (2.79) we obtain an additive contribution to the average rate of change of the thermodynamic entropy of the electronic subsystem

$$\langle \partial_t \hat{\mathcal{S}}_t \rangle_{\text{el}} = - \sum_{k, n_k} (\partial_t p_{n_k}) \ln p_{n_k} = - \sum_k (\partial_t f_k) \ln \frac{f_k}{1 - f_k}, \quad (2.83)$$

where in the last equality we identify the nonequilibrium one-electron distribution as $f_k = \sum_{n_k} n_k p_{n_k} = p_{n_k=1}$ and use $\sum_{n_{k'}} p_{n_{k'}} = 1$ to express $p_{n_k=0} = 1 - f_k$. The transport equation for f_k is obtained by multiplying (2.80) by n_k and summing over all n . To this end, note that

$$\Gamma_{nn'} = \sum_{k, k' (k \neq k')} w_{kk'} n_k (1 - n_{k'}) |\langle \dots n_{k'} - 1 \dots n_k + 1 \dots | n' \rangle|^2, \quad (2.84)$$

which is obtain by using (2.65) explicitly, where the one-electron transition rate from state k to state k' is

$$w_{kk'} = 2\pi \sum_q |M_{k'k}^q|^2 \left[\bar{N}(\omega_q) \delta(\epsilon_{k'} - \epsilon_k - \omega_q) + [1 + \bar{N}(\omega_q)] \delta(\epsilon_{k'} - \epsilon_k + \omega_q) \right], \quad (2.85)$$

with $\bar{N}(\omega_q) = \sum_N P_N^{\text{ph}} \langle N | \hat{a}_q^\dagger \hat{a}_q | N \rangle$ the average number of phonons in the single-particle state with quantum number q . We assume that the phonon subsystem can be kept in equilibrium at temperature T (hence the dependence of \bar{N} on ω_q only), no matter the nonequilibrium state of the electrons, as is the case for a good enough heat reservoir.

That the phonons can be considered as a heat reservoir in the Born-Oppenheimer approximation can be seen by looking at the transport equation for the phonon subsystem, obtained from (2.76) by summing over n

$$\partial_t P_N^{\text{ph}} = \sum_{N'} (P_{N'}^{\text{ph}} \Theta_{N'N} - P_N^{\text{ph}} \Theta_{NN'}), \quad (2.86)$$

where we have defined the electron-averaged reduced transition rates as

$$\Theta_{NN'} = \sum_n P_n^{\text{el}} \sum_{n'} W_{nN,n'N'}. \quad (2.87)$$

Here we observe the important fact that the contribution from the first term of (2.76) vanishes due to the null value of the trace of the commutator $[\hat{H}_F, \hat{\rho}_0]$ in the subspace of electrons. This allows the existence of a steady state solution of (2.86) for which detailed balance holds, which is then an equilibrium solution. In any case, the assumption that the phonons are in equilibrium is not necessary for the following derivation of the electronic entropy production, as $\bar{N}(\omega_q)$ in (2.85) can be replaced by the more complicated average obtained by using the nonequilibrium solution of (2.86), not investigated here.

The transport equation for the one-electron distribution is then found to be, from (2.80)

$$\partial_t f_k = \frac{1}{i} \sum_{nN} n_k (L_F \hat{\rho}_0)_{nN,nN} + \sum_{nn'} n_k (P_{n'}^{\text{el}} \Gamma_{n'n} - P_n^{\text{el}} \Gamma_{nn'}). \quad (2.88)$$

This is just the quantum Boltzmann equation. To write it in the familiar form we first note that, by writing \hat{H}_{el} in first-quantized form and using the well-known formula $[\hat{\mathbf{x}}_e, f(\hat{\mathbf{p}}_e)] = i \nabla_{\hat{\mathbf{p}}_e} f(\hat{\mathbf{p}}_e)$ we have $L_F \hat{\rho}_0 = i(e/T) \mathbf{E} \cdot \hat{\mathbf{v}} \hat{\rho}_0$, where $\hat{\mathbf{v}} = \sum_e (\hat{\mathbf{p}}_e/m) = \sum_k \mathbf{v}_k \hat{c}_k^\dagger \hat{c}_k$ is the velocity operator of all electrons, with $\mathbf{v}_k = \nabla_k \epsilon_k$ the band velocity. Therefore, the first term in (2.88) is

$$\begin{aligned} (\partial_t f_k)_{\text{drift}} &= \frac{1}{i} \sum_{nN} n_k (L_F \hat{\rho}_0)_{nN,nN} = \frac{e\mathbf{E}}{T} \cdot \text{Tr}(\hat{n}_k \hat{\mathbf{v}} \hat{\rho}_0), \\ &= e\mathbf{E} \cdot \mathbf{v}_k f_k^0 (1 - f_k^0)/T = -e\mathbf{E} \cdot \nabla_k f_k^0, \end{aligned} \quad (2.89)$$

where $f_k^0 = \text{Tr}(\hat{n}_k \hat{\rho}_0)$ is the equilibrium Fermi-Dirac one-electron distribution. The

second term in (2.88) can be written, using (2.84), as

$$\begin{aligned}
(\partial_t f_k)_{\text{coll}} &= \sum_{nn'} n_k (P_n^{\text{el}} \Gamma_{n'n} - P_n^{\text{el}} \Gamma_{nn'}), \\
&= \sum_n P_n^{\text{el}} n_k \sum_{k',k''} w_{k'k''} (1 - n_{k'}) n_{k''} - \sum_n P_n^{\text{el}} n_k \sum_{k',k''} w_{k'k''} n_{k'} (1 - n_{k''}).
\end{aligned} \tag{2.90}$$

Therefore, by noting that $n_k(1 - n_k) = 0$ and using (2.82) we see that the terms which do not cancel in the above sums are

$$(\partial_t f_k)_{\text{coll}} = \sum_{k'} [f_{k'} w_{k'k} (1 - f_k) - f_k w_{kk'} (1 - f_{k'})]. \tag{2.91}$$

We have thus arrived to the familiar form of the quantum Boltzmann equation by substituting (2.89) and (2.91) into (2.88). With this, we can rewrite the average rate of change of the thermodynamic entropy of the electronic subsystem, from (2.83), as

$$\langle \partial_t \hat{\mathcal{S}}_t \rangle_{\text{el}} = \Pi_{\text{el}} - \Phi_{\text{el}}, \tag{2.92}$$

which is the entropy balance equation for the electronic subsystem, with the average electronic entropy production rate

$$\Pi_{\text{el}} = \frac{1}{2} \sum_{kk'} [f_{k'} w_{k'k} (1 - f_k) - f_k w_{kk'} (1 - f_{k'})] \ln \frac{f_{k'} w_{k'k} (1 - f_k)}{f_k w_{kk'} (1 - f_{k'})}, \tag{2.93}$$

which, similar to (2.55), is a sum of terms of the form $(x - y) \ln(x/y)$ and then satisfies the second law of thermodynamics; and the entropy flux from the electrons to the phonons is

$$\Phi_{\text{el}} = \frac{1}{2} \sum_{kk'} [f_{k'} w_{k'k} (1 - f_k) - f_k w_{kk'} (1 - f_{k'})] \ln \frac{w_{k'k}}{w_{kk'}} + \sum_k (\partial_t f_k)_{\text{drift}} \ln \frac{f_k}{1 - f_k}. \tag{2.94}$$

In the steady state the left-hand side of (2.92) is exactly zero and then all the entropy produced in the electronic system is transported to the phonons. We now want to show that this steady-state entropy flux toward the lattice vibrations gives the expression of the well-known Joule heating.

We need a solution, $f_k = f_k^0 + \delta f_k$, of the quantum Boltzmann equation which, to linear order in the electric field strength, we write formally as

$$\delta f_k = \sum_{k'} \mathcal{W}_{kk'}^{-1} \left[\frac{e\mathbf{E} \cdot \mathbf{v}_{k'}}{T} f_{k'}^0 (1 - f_{k'}^0) \right], \quad (2.95)$$

where the linearized collision operator \mathcal{W} , has matrix elements

$$\mathcal{W}_{kk'} = f_k^0 w_{kk'} + w_{k'k} (1 - f_k^0) - \frac{\delta_{kk'}}{\tau_k}. \quad (2.96)$$

The quasiparticle relaxation time τ_k is given by

$$\frac{1}{\tau_k} = \sum_{k'} [f_{k'}^0 w_{k'k} + w_{kk'} (1 - f_{k'}^0)], \quad (2.97)$$

and becomes equal to the momentum relaxation time if the transition rates $w_{kk'}$ are independent of the angle between k and k' .

We now expand (2.93). Because both the logarithm and the prefactor vanish in equilibrium the leading contribution is $O(\delta f)^2$. The term from expanding the logarithm is easily seen to be

$$\frac{\delta f_{k'}}{f_{k'}^0 (1 - f_{k'}^0)} - \frac{\delta f_k}{f_k^0 (1 - f_k^0)},$$

while the term coming from the prefactor is

$$\mathcal{W}_{kk'} \delta f_{k'} - \mathcal{W}_{k'k} \delta f_k. \quad (2.98)$$

Combining these equations with (2.95) yields an expression for $\pi_{\text{el}} = \Pi_{\text{el}}/\Omega$, the electronic entropy production per unit of volume Ω of the material,

$$\pi_{\text{el}} = \frac{1}{\Omega} \sum_k \frac{e\mathbf{E} \cdot \mathbf{v}_k}{T} \delta f_k = \frac{\sigma E^2}{T}, \quad (2.99)$$

where, in the last equality, we recognize the electric current density as $(1/\Omega) \sum_k e\mathbf{v}_k \delta f_k = \sigma \mathbf{E}$, with σ the electric conductivity.

$$\sigma = -\frac{e^2}{\Omega} \sum_k (\hat{\mathbf{E}} \cdot \mathbf{v}_k)^2 \tau_k \frac{\partial f_k^0}{\partial \epsilon_k}. \quad (2.100)$$

Thus we see that to leading order in the electron-phonon coupling and the electric field, and on the assumption that the phonons act as a reservoir, the electronic entropy production predicted by our formula is exactly the result expected from the Joule heating, $T\pi_{\text{el}} = \sigma E^2$, implied by the electric field. Therefore, as desired, we have arrived at an expression of energy dissipation from a first-principle calculation of entropy production, not the other way around, as in previous approaches.

We remark that the results for the entropy production presented here are beyond the linear response theory. This is because, even when starting from the linear in the electric field correction to the density matrix, $\hat{\rho}_{1,t}$ (see Eq. (2.71)), we derived the leading contribution to the electronic entropy production which is quadratic in the electric field. This is in contrast to past approaches [Kohn and Luttinger \(1957\)](#); [Suzuki \(2012\)](#) for the calculation of the Joule heating, which requires going to the second order in the electric field contribution to the density matrix $\hat{\rho}_{2,t}$ for the calculation of the rate of change of the energy of the electrons. A field-theoretic approach [Rammer and Smith \(1986\)](#); [Rammer \(2007\)](#) for the calculation of higher order terms in the entropy production, beyond the Born-Markov approximation will be treated elsewhere.

It is illustrative to evaluate the result explicitly, assuming e.g. dispersionless

optical phonons $\omega_q = \omega_0$. With $|M_{k'k}^q|^2 = M \delta_{q,k'-k}$, and assuming a degenerate electron system (i.e. $T \ll \epsilon_F$) we obtain

$$\Pi_{\text{el}} = \frac{(e^2 E^2 / 3\pi m M) D_{\epsilon_F}}{D_{\epsilon_F - \omega_0} + D_{\epsilon_F + \omega_0}} (\epsilon_F / T) \sinh(\omega_0 / T), \quad (2.101)$$

with D_ϵ the electron density of states. In this case, the entropy production becomes large at low temperatures due to an increase in the conductivity (phonons not thermally activated and then scarcity of scattering centers), and hence in the Joule heating; this is expected when the only scattering mechanism is from optical phonons.

Finally, we would like to point out the connection of the result (2.99) with the discussion in section 2.4 concerning the foundations of the classical theory. With only the action of one of the subsystems (the sources of the \mathbf{E} -field) treated parametrically, with the three spatial components of the field E_λ playing the role of the external parameters to the electronic subsystem, we can define an operator $\hat{F}_\lambda = \partial \hat{H}_F / \partial E_\lambda$ for the force exerted on the electrons upon variation of the field and write

$$\begin{aligned} T \hat{\Pi}_{\text{el}} &= \sum_\lambda \hat{F}_\lambda \partial_t E_\lambda = \partial_t \sum_\lambda \hat{F}_\lambda E_\lambda - \sum_\lambda (\partial_t \hat{F}_\lambda) E_\lambda \\ &= \partial_t \hat{H}_F + e \hat{\mathbf{v}} \cdot \mathbf{E} = e \hat{\mathbf{v}} \cdot \mathbf{E}, \end{aligned} \quad (2.102)$$

where $\hat{H}_F = -e \sum_{\lambda,e} E_\lambda \hat{x}_e^\lambda$, and to get the last equality we use $\partial_t \hat{H}_F = \partial_t \hat{H} = 0$, since the total system is isolated. Taking expectation value of (2.102), the last equality is just (2.99) and the form of the first equality is reminiscent of the classical expression (2.29).

We then see that, although in the present discussion the subsystems are not separated by spatial boundaries (the essence of the generalized thermodynamic description) and there is no local equilibrium at all times: the phonons remain in equilibrium, as implied by the assumption that they constitute a good heat reservoir, but the electrons attain a nonequilibrium steady state; the common feature with the discussion in

section 2.4 is the complete factorization of the probability distribution of the system over the degrees of freedom of the different subsystems (uncorrelated subsystems), here manifested as the Born-Oppenheimer approximation. An appropriate account of the quantum correlations between subsystems is therefore the key to purely quantum thermodynamic behavior.

2.8 Summary

We have developed a theory for the entropy production in quantum many-body systems by introducing an entropy operator and calculating the average rate of change of its thermodynamically measurable part. We show that the laws of thermodynamics are satisfied exactly within our formalism. In the Born-Markov approximation which describes the physics of weakly-coupled subsystems of an isolated system in the long-time limit, the theory reproduces the entropy balance equation which is fundamental in classical nonequilibrium thermodynamics and the Joule heating contribution to the entropy production expected in a standard conductor.

PHYSICAL REVIEW B **93**, 224305 (2016)**Theory of entropy production in quantum many-body systems**

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(Received 16 September 2015; revised manuscript received 16 May 2016; published 29 June 2016)

We define the entropy operator as the negative of the logarithm of the density matrix, give a prescription for extracting its thermodynamically measurable part, and discuss its dynamics. For an isolated system we derive the first, second, and third laws of thermodynamics. For weakly coupled subsystems of an isolated system, an expression for the long-time limit of the expectation value of the rate of change of the thermodynamically measurable part of the entropy operator is derived and interpreted in terms of entropy production and entropy transport terms. The interpretation is justified by comparison to the known expression for the entropy production in an aged classical Markovian system with Gaussian fluctuations and by a calculation of the current-induced entropy production in a conductor with electron-phonon scattering.

DOI: [10.1103/PhysRevB.93.224305](https://doi.org/10.1103/PhysRevB.93.224305)**I. INTRODUCTION**

Attempts to show how nonequilibrium thermodynamic behavior emerges from the underlying quantum mechanics of individual particles is now being dubbed quantum thermodynamics [1–4]. Several approaches have arisen, revealing important aspects in this endeavor, such as how thermal fluctuations and external driving mechanisms affect the stochastic course of nonequilibrium processes of small systems [5], which has led to fluctuation theorems [6–8] going beyond the results from the Kubo linear response theory, as well as generalized fluctuation-dissipation relations as studied in isolated quantum systems after a quench [9–11]. Other aspects, more in the spirit of traditional nonequilibrium statistical mechanics [12], include thermalization in isolated quantum systems [13–17] and the establishment of steady states in open quantum systems [18–24]. A unified treatment along the lines of the classical theory of nonequilibrium thermodynamics is of crucial importance for a clear identification of the quantum-to-classical correspondence and the new features brought about by fully quantum-mechanical nonequilibrium behavior.

The remarkable success of the classical theory [25–28] in the description of macroscopic phenomena in fluids motivates us to ask what the basic ingredients of this formalism are that such a unified treatment of quantum thermodynamics must also contain. We recall that the building blocks of the classical theory are (i) macroscopic observables, explicitly defined as a set of thermodynamically measurable or slowly varying quantities, (ii) conservation laws for these variables, and, as a foundational pillar, (iii) an entropy balance equation, splitting the rate of change of entropy as a part which is irreversibly produced, in accordance with the second law of thermodynamics, and a part which is transported. The validity of this theory relies on the *local equilibrium* assumption, whereby the nonequilibrium thermodynamic entropy is considered locally as a function of the same extensive variables as in equilibrium.

Although significant attempts to give meaning to entropy out of equilibrium [29] have long been known in quantum statistics [30–34], a complete theory of quantum entropy production has not been provided yet. The main problem is how to conceive an adequate quantum entropy balance equation without assuming local equilibrium.

For an isolated system, there is no entropy to be transported outside the system, and hence, the entropy balance equation reduces to finding the right quantum expression for entropy whose rate of change is non-negative, according to the second law of thermodynamics, this rate then being the entropy production. Important efforts have been devoted to obtain such an expression from the density matrix [12,35,36], but the third law of thermodynamics, involving the vanishing entropy of pure states, has not been satisfactorily established.

On the other hand, for a subsystem of an isolated system the establishment of a quantum entropy balance equation has been partially addressed [37–43] by assuming that the rate of change of an adopted expression for the nonequilibrium entropy of the subsystem, obtained from the reduced density matrix, is directly connected, as in the classical theory, to the rate of change of its energy. This involves the identification of a microscopic expression for heat which is not unique [44] and therefore quite problematic but, most importantly, does not constitute a full deviation from the local equilibrium assumption, as we show later.

The purpose of this paper is to provide a more general treatment of quantum entropy production and then lay the foundation of a unified theory of quantum thermodynamics in close correspondence to the classical theory. We introduce a thermodynamic entropy operator \hat{S}_t for isolated quantum many-body systems and show that the rate of change of its expectation value is non-negative, according to the second law of thermodynamics. Unlike previous approaches, we establish the third law of thermodynamics as a well-defined vanishing of the thermodynamic entropy for pure states.

The quantum entropy balance equation for a given subsystem of an isolated system is obtained by first studying the time evolution of $\langle \partial_t \hat{S}_t \rangle$ for the isolated system from first principles, i.e., from the Liouville–von Neumann equation for the density matrix, using the standard generalized master equation approach of nonequilibrium statistical mechanics [45–49], and by subsequently making reasonable assumptions regarding the factorization properties of the nonequilibrium probability distribution of microscopic states over the degrees of freedom of the different subsystems.

We restrict ourselves here to weakly coupled subsystems to show how our theory is consistent with the classical theory, to elucidate the manner in which the local equilibrium

approximation can be fully abandoned, and to pave the way to study cases of strong coupling between subsystems for which the aforementioned factorization properties of the probability distribution of microscopic states become the main subject of study, marking a deep connection with quantum information theory. A detailed investigation of a methodology to approach these cases will be considered elsewhere.

The pursuit of the so-outlined research program is essential both for a more fundamental understanding of nonequilibrium behavior [50] and because entropy production is inherent to dissipation so that a good atomic-scale description may have technological impact, e.g., by enabling better control of waste heat and thermoelectric effects in single-molecule electronics [51–53] and guiding the efficient design of quantum refrigerators [54] and quantum heat machines [55], nanosized photoelectric devices [56], nanothermoelectric engines [57,58] based on quantum dots, etc., which are envisioned as practical applications of quantum thermodynamics.

It turns out, as we show here with a particular example of electronic conduction in the presence of phonon modes playing the role of a reservoir, that our theory gives an explicit expression for the Joule heating from a calculation of the steady-state electronic entropy production alone. This represents an important progress since this is done without calculating the rate of change of the energy of the electron subsystem.

This paper is organized as follows: in Sec. II we give a brief review of entropy production and the second law of thermodynamics as they manifest in phenomenological thermodynamics. In Sec. III we discuss the local equilibrium assumption from a quantum perspective, with a derivation of the first law of thermodynamics from the expression for $\langle \partial_t \hat{S}_I \rangle$ in this case, which is shown to hold for *quasistatic* transformations or slow processes. This section, which mainly discusses how the foundations of the classical theory are to be understood quantum mechanically, serves as a motivation to introduce the operator $\partial_t \hat{S}_I$ for general isolated quantum systems that include possible reservoirs.

A transition is made in Sec. IV to the generalized thermodynamic description of quantum systems. The second and third laws of thermodynamics are established here for any isolated system, and an entropy balance equation is derived, splitting $\langle \partial_t \hat{S} \rangle$ into entropy production and entropy transport terms. In Sec. V, we show how the theory is consistent with Onsager’s classical stochastic entropy production in an aged system. Finally, in Sec. VI we calculate the electronic entropy production in a simple metal consisting of independent electrons weakly coupled to phonons in the presence of an external electric field, deriving the Joule heating, and we conclude with Sec. VII.

II. ENTROPY PRODUCTION IN PHENOMENOLOGICAL THERMODYNAMICS

The thermodynamic definition of entropy *changes* for any kind of process in a closed system (not interchanging particles with the reservoirs) was given by Clausius at the very end of his monumental 1865 paper [59,60]. If the system, which is considered to be in contact with a set of heat sources at different temperatures T , follows a path γ in the space of

thermodynamic states, joining the initial and final arbitrary states A and B , respectively, then the thermodynamic entropy change in the process is

$$S_B - S_A = N_C[\gamma] + \int_A^B (\delta Q/T)_\gamma, \quad (1)$$

where δQ is an infinitesimal amount of heat absorbed from (or surrendered to) the heat source at temperature T and the quantity $N_C[\gamma]$, representing what came to be known as the “uncompensated heat of Clausius” [61], is a functional of the process. Clausius defined it in such a way that

$$N_C[\gamma] \equiv - \oint_\gamma \delta Q/T = - \int_A^B (\delta Q/T)_\gamma - \int_B^A (\delta Q/T)_{\gamma_R}, \quad (2)$$

where γ_R is an arbitrary *reversible* path which is “imagined” to bring the system back to its initial state A . He proved that

$$N_C[\gamma] \geq 0, \quad (\text{Clausius inequality}), \quad (3)$$

for any γ , which was a generalization of Carnot’s results for cyclic processes; the equality holds if and only if γ is a reversible path. This is the starting point of all the discussions found in textbooks of the second law of thermodynamics [62] and is therefore regarded here as the fundamental expression for this law.

A classical formulation of nonequilibrium thermodynamics has been founded [25,26] by taking as a starting point (1) written in differential form and generalized to apply locally in small-volume elements δv of a system,

$$dS = d_i S + d_e S, \quad (4)$$

where $d_i S \equiv dN_C$ is the entropy produced during an infinitesimal time interval due to irreversible processes taking place inside the volume element and $d_e S$ is the entropy supplied by its surroundings ($\equiv \delta Q/T$ for a closed element). The second law of thermodynamics requires only that the entropy produced satisfies

$$d_i S \geq 0, \quad (\text{Clausius inequality}). \quad (5)$$

The theory so obtained for the phenomenological entropy production, $\Pi_{\delta v} = d_i S/dt$, successfully describes *slow* processes or phenomena where the decay time of local perturbations is very short compared to the global relaxation time, as in chemical reactions, diffusion processes, heat conduction, and their cross effects in gases and liquids. However, it requires fundamental modifications for *fast* processes [27,28], and in the following, we argue from a quantum-mechanical perspective why this happens to be the case, setting the stage and motivating the method for the subsequent development of our theory.

III. LOCAL EQUILIBRIUM AND QUASISTATIC QUANTUM TRANSFORMATIONS

Consider an isolated macroscopic system, possibly containing a set of particle and heat reservoirs which is divided into macroscopic subsystems. Microscopically, the total system is

defined by the Hamiltonian

$$\hat{H} = \sum_l \hat{H}_l + \sum_{l < m} \hat{H}_{lm}, \quad (6)$$

where \hat{H}_l is the Hamiltonian of subsystem l , involving the kinetic energies of the particles comprising the subsystem as well as the energy of interaction among all these particles, and \hat{H}_{lm} is the Hamiltonian representing the interactions among the particles of subsystem l with those of subsystem m , possibly including hopping terms allowing particle transfer.

The fundamental assumption of statistical mechanics [63] is that, since the interaction energy among the parts scales with their common surface areas, while the energy of the parts scales with their respective volumes, we can then remove all \hat{H}_{lm} in Eq. (6) from a *macroscopic* description of the dynamics and introduce instead a set of time-dependent parameters $\{x_\lambda^l\}$ embodying macroscopic constraints for the subsystem l that evolve in time due to changes in the other subsystems. The operator representing macroscopic energy measurements in this approximation is

$$\hat{\mathcal{H}} = \sum_l \hat{\mathcal{H}}_l, \quad \hat{\mathcal{H}}_l = \hat{H}_l(\{x_\lambda^l\}), \quad (7)$$

where the notation in Eq. (7) indicates that $\hat{\mathcal{H}}_l$ is to be taken as \hat{H}_l plus an external potential due to the other subsystems and represented *parametrically*. For instance, a quantum subsystem acted upon by an external electric field is seen in the description of (6) as having a Coulomb potential energy (operator) coupling all the charges of the subsystem with all the charges outside of it which are sources of this field, while in the approximate description of (7), it is seen as being coupled to an external parameter E representing the strength of the field. We shall call the latter the *thermodynamic* description.

The local equilibrium assumption in the thermodynamic description is the statement that the macroscopic state of each part of our system, with a number of particles operator \hat{N}_l , a temperature T_l , and a chemical potential μ_l , is an equilibrium state. The local equilibrium density matrix of the total system is the factorized Gibbs state (subsystems macroscopically uncorrelated)

$$\hat{\rho}^r = \bigotimes_l \hat{\rho}_l^r = \bigotimes_l \exp[-(\hat{\mathcal{H}}_l - \mu_l \hat{N}_l - \Omega_l)/T_l], \quad (8)$$

with $\Omega_l = \Omega_l(T_l, \mu_l, \{x_\lambda^l\})$ being the thermodynamic potential of subsystem l , introduced so as to normalize the density matrix, that is, $\text{Tr} \exp[-(\hat{\mathcal{H}}_l - \mu_l \hat{N}_l)/T_l] = \exp(-\Omega_l/T_l)$. Note that, since the degrees of freedom of different subsystems are *uncoupled* in the thermodynamic description, all operators $\hat{\mathcal{H}}_l$ and \hat{N}_m form a mutually commuting set and then define a natural basis of common eigenstates that we represent as $\{|\alpha\rangle\}$.

The appearance of this natural set defines a family of observables acting on the system Hilbert space that, like $\hat{\mathcal{H}}_l$ and \hat{N}_m , we call thermodynamic; these observables are diagonal in the basis $\{|\alpha\rangle\}$. According to this, $\hat{\mathcal{H}}$ is a thermodynamic observable, and we denote the set of all these operators as

$$\mathcal{T} = \{\hat{\mathcal{G}} : [\hat{\mathcal{G}}, \hat{\mathcal{H}}] = 0\}. \quad (9)$$

Clearly, all constant operators as well as all time-averaged observables [32,64] belong to this family. With \mathcal{D} denoting

the projection operator to the subspace spanned by $\{|\alpha\rangle\}$, we can then split an arbitrary observable \hat{G} in the convenient form

$$\hat{G} = \mathcal{D}\hat{G} + \mathcal{N}\hat{G} = \hat{\mathcal{G}} + \hat{\mathcal{G}}^\sim, \quad (10)$$

where $\hat{\mathcal{G}} = \mathcal{D}\hat{G}$ is the thermodynamically measurable part (or thermodynamic part) of \hat{G} , with the complementary part being $\hat{\mathcal{G}}^\sim = \mathcal{N}\hat{G} = \hat{G} - \hat{\mathcal{G}}$.

The thermodynamic observables must have the characteristic of being slowly varying quantities [65–68]. This is quantified in our theory by introducing a geometric measure Δ of how approximate the thermodynamic description is. For this, let us introduce for an arbitrary observable \hat{B} the Hermitian operator

$$\hat{C}_{AB} = -i[\hat{A}, \hat{B}], \quad \hat{A} \in \mathcal{T}, \quad (11)$$

and consider the simple geometry induced by the Hilbert-Schmidt norm $\|\hat{C}_{AB}\| = (\text{Tr} \hat{C}_{AB}^\dagger \hat{C}_{AB})^{1/2}$. It is trivially seen that

$$\|\hat{C}_{\mathcal{H}0}\| = \|\hat{C}_{\mathcal{G}0}\| = 0, \quad (12)$$

and by using the Jacobi identity for commutators, together with $[\hat{\mathcal{G}}, \hat{\mathcal{H}}] = 0$, coming from (9), we can write

$$\|\hat{C}_{\mathcal{H}\hat{\mathcal{G}}}\| = \|\hat{C}_{\mathcal{G}\mathcal{H}\mathcal{H}}\|, \quad (13)$$

where we identify $\hat{\mathcal{G}} = \hat{C}_{GH}$ when the parameters representing external constraints are fixed in time. Therefore, if $\hat{C}_{\mathcal{H}\mathcal{H}}$ tend to the null operator in the norm, i.e., if we have $\Delta \rightarrow 0$ with

$$\Delta^2 = \varepsilon_0^{-4} \|\hat{C}_{\mathcal{H}\mathcal{H}}\|^2 = \varepsilon_0^{-4} \sum_{\alpha\alpha'} (\varepsilon_\alpha - \varepsilon_{\alpha'})^2 |\langle \alpha | \hat{H} | \alpha' \rangle|^2, \quad (14)$$

where $\hat{\mathcal{H}}|\alpha\rangle = \varepsilon_\alpha|\alpha\rangle$ and ε_0 is the smallest characteristic energy in the system (making Δ dimensionless), then we conclude, by using (12) and (13) as well as the continuity of the norm, that the quality of slow variation can be expressed as

$$\|\hat{\mathcal{G}}\| = \|[\hat{\mathcal{G}}, \hat{H}]\| = O(\Delta). \quad (15)$$

The condition $\Delta \rightarrow 0$ is physically realized when the thermodynamic limit is taken for all the subsystems comprising the total system since in this limit $\langle \hat{H} \rangle$ and $\langle \hat{\mathcal{H}} \rangle$ tend to be indistinguishable for arbitrary states.

We now give the steps that constitute our general method in the next section. Given the density matrix $\hat{\rho}_t$ of the total system, we define the entropy operator as the negative of its logarithm, $\hat{S}_t = -\ln \hat{\rho}_t$, and, from this and the aforementioned discussion, the *thermodynamic* entropy operator as $\hat{S}_t = \mathcal{D}\hat{S}_t$. Since in the local equilibrium approximation the density matrix $\hat{\rho}_t = \hat{\rho}^r$ is already diagonal in the basis $\{|\alpha\rangle\}$, we have in this case

$$\hat{S}^r = -\ln \hat{\rho}^r = \frac{1}{T_l} \sum_l (\hat{\mathcal{H}}_l - \mu_l \hat{N}_l - \Omega_l), \quad (16)$$

where we have used the commutativity of all $\hat{\mathcal{H}}_l$ and \hat{N}_m to express $\ln \hat{\rho}^r = \sum_l \ln \hat{\rho}_l^r$. We are interested in thermodynamic entropy changes as the main observable, so the next step is an expression for $\langle \partial_t \hat{S}_t \rangle$, which we get by first

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differentiating (16),

$$d\hat{S}^r = \sum_l \frac{1}{T_l} \left[d\hat{\mathcal{H}}_l - d\mu_l \hat{\mathcal{N}}_l - \mu_l d\hat{\mathcal{N}}_l - d\Omega_l - \frac{dT_l}{T_l} (\hat{\mathcal{H}}_l - \mu_l \hat{\mathcal{N}}_l - \Omega_l) \right]. \quad (17)$$

Since Ω_l is a function of μ_l , T_l and of the external parameters x_λ^l implicit in $\hat{\mathcal{H}}_l$, we can differentiate the normalization relation $\text{Tr} \exp[-(\hat{\mathcal{H}}_l - \mu_l \hat{\mathcal{N}}_l)/T_l] = \exp(-\Omega_l/T_l)$ after variations in these arguments to get, after noting that $\langle \hat{G}_l \rangle = \text{Tr} \hat{\rho}^r \hat{G}_l = \text{Tr} \hat{\rho}_l^r \hat{G}_l$ for a local operator \hat{G}_l acting on the l th subsystem,

$$d\Omega_l = - \sum_\lambda F_\lambda^l dx_\lambda^l - \langle \hat{\mathcal{N}}_l \rangle d\mu_l - \frac{dT_l}{T_l} (\langle \hat{\mathcal{H}}_l \rangle - \mu_l \langle \hat{\mathcal{N}}_l \rangle - \Omega_l), \quad (18)$$

with $F_\lambda^l = -\langle \partial \hat{\mathcal{H}}_l / \partial x_\lambda^l \rangle$ being the average force exerted by subsystem l on its surroundings to get the displacements dx_λ^l . Taking the expectation value of (17) and substituting (18), we conclude that the average rate of change of the total thermodynamic entropy is, in this case, additive, $\langle d\hat{S}^r \rangle = \sum_l \langle d\hat{S}_l^r \rangle$, with

$$T_l \langle d\hat{S}_l^r \rangle = \langle d\hat{\mathcal{H}}_l \rangle - \mu_l \langle d\hat{\mathcal{N}}_l \rangle + \sum_\lambda F_\lambda^l dx_\lambda^l. \quad (19)$$

We have arrived in this way at the first law of thermodynamics, through a line of reasoning originally due to Gibbs [69], generalized here to the quantum case.

Note that for an arbitrary observable \hat{G} , the identity $\langle d\hat{G}/dt \rangle = \partial \langle \hat{G} \rangle / \partial t$ holds whenever the density matrix used to calculate the expectation value satisfies the Liouville–von Neumann equation, as is easily proved by changing to the Heisenberg picture within the expectation value operation, where $d\hat{G}/dt = \partial \hat{G} / \partial t - i[\hat{G}, \hat{H}]$, with \hat{G} depending explicitly on time in the Schrödinger picture via the external parameters, and using the known identity $\text{Tr} \hat{A}[\hat{B}, \hat{C}] = \text{Tr} \hat{C}[\hat{A}, \hat{B}]$. Therefore, *as long as* the local equilibrium density matrix $\hat{\rho}^r$ satisfies the Liouville–von Neumann equation, we can commute the operation $\langle d\hat{G} \rangle = \partial \langle \hat{G} \rangle$ and write (19) as the usual form of the first law of thermodynamics.

The equivalence of (19) to the usual form of the first law of thermodynamics

$$T_l \partial_t \langle \hat{S}_l^r \rangle = \partial_t \langle \hat{\mathcal{H}}_l \rangle - \mu_l \partial_t \langle \hat{\mathcal{N}}_l \rangle + \sum_\lambda F_\lambda^l \partial_t x_\lambda^l \quad (20)$$

then requires that $\hat{\rho}^r$ satisfies the Liouville–von Neumann equation $i \partial_t \hat{\rho}^r = [\hat{H}, \hat{\rho}^r]$, where we use the symbol ∂_t as a shorthand notation for $\partial/\partial t$. For this to be the case, it is necessary from (15) that

$$\|\partial_t \hat{\rho}^r\| = O(\Delta) \quad (21)$$

since $\hat{\rho}^r$ is expressed in terms of thermodynamic observables. When the thermodynamic limit is taken for each subsystem, we have $\Delta \rightarrow 0$, and then the parameters x_λ^l should vary with time so slowly that the state $\hat{\rho}^r$ can be interpreted as “moving” in a locus of equilibrium states, so that $\|\partial_t \hat{\rho}^r\| \rightarrow 0$ in Eq. (21). These are precisely the *quasistatic* (or reversible) transformations for which the first law involving thermodynamic

entropy changes applies, hence the superscript r standing for reversible and the systematic omission of the time subindex in the variables. Note that in this case, the quantity $N_C[\gamma]$ in Eq. (1) vanishes for any $\gamma = \{x_\lambda^l(t), \forall \lambda, l \text{ and } t \in [t_A, t_B]\}$.

A nonzero entropy production appears instead when the subsystems are macroscopic at the atomic scale, but compared to the size of the total system, they are small-volume elements δv_l . In this case, an entropy balance equation may be obtained from (20) by using the relations

$$\partial_t \langle \hat{\mathcal{H}}_l \rangle = - \sum_m J_{\mathcal{H}}^{lm} + \sum_\lambda \frac{\partial \langle \hat{\mathcal{H}}_l \rangle}{\partial x_\lambda^l} \partial_t x_\lambda^l, \quad (22)$$

$$\partial_t \langle \hat{\mathcal{N}}_l \rangle = - \sum_m J_{\mathcal{N}}^{lm} + \sum_\lambda \frac{\partial \langle \hat{\mathcal{N}}_l \rangle}{\partial x_\lambda^l} \partial_t x_\lambda^l, \quad (23)$$

which state that the average macroscopic energy and number of particles of a given subsystem can only change by transport to other subsystems, defining the corresponding currents $J_{\mathcal{H}}^{lm}$ and $J_{\mathcal{N}}^{lm}$ in terms of quantities proportional to the particle velocities, with an appropriate microscopic account for the heat currents, plus terms allowing the technical possibility of the creation or destruction of particles induced by the variation of the external constraints. Substituting these in Eq. (20), we get

$$\begin{aligned} \partial_t \langle \hat{S}_l^r \rangle &= \frac{1}{T_l} \sum_\lambda \left[\frac{\partial}{\partial x_\lambda^l} (\langle \hat{\mathcal{H}}_l \rangle - \mu_l \langle \hat{\mathcal{N}}_l \rangle) + F_\lambda^l \right] \partial_t x_\lambda^l \\ &\quad - \frac{1}{T_l} \sum_m (J_{\mathcal{H}}^{lm} - \mu_l J_{\mathcal{N}}^{lm}) = \Pi_{\delta v_l} - \Phi_{\delta v_l}, \end{aligned} \quad (24)$$

with the first term in the first equality being the entropy production term $\Pi_{\delta v_l}$ and the second one being the entropy transport term $\Phi_{\delta v_l}$. Results consistent with the classical theory are obtained when particle creation or destruction is not observed macroscopically, in which case (22) and (23) are just the usual conservation laws (continuity equations) and the entropy production in the subsystem reduces to the well-known sum of products of thermodynamic forces times the rate of change of their conjugate external parameters

$$\Pi_{\delta v_l} = \frac{1}{T_l} \sum_\lambda F_\lambda^l \partial_t x_\lambda^l, \quad (\text{classical}). \quad (25)$$

The presentation given here can be straightforwardly generalized by considering local equilibrium Gibbs ensembles more general than (8), that is, by augmenting the thermodynamic entropy operator (16) with terms proportional to the components of the macroscopic linear and angular momentum operators of each subsystem [63], with (22) and (23) expanded to include the conservation laws of their respective expectation values.

Note that we have kept the superscript r (although not strictly with its original connotation) in Eq. (24) because, even though the thermodynamic limit is not taken for each subsystem, which would make $\Delta \rightarrow 0$ and the processes necessarily quasistatic, the fact that the volume elements δv_l are macroscopic at the atomic scale still implies that Δ is very small and hence, from (21), that the variations $\partial_t \hat{\rho}^r$ should correspondingly be very small in the norm. As mentioned in Sec. II, we then see why the classical theory works well for *slow* processes, i.e., those for which the time to get relaxation

to equilibrium within each volume element is much shorter than the time to get equilibrium among them.

The discussion in this section elucidates the problems with the local equilibrium assumption and previous theories of entropy production, which rely on expressions of the type (20) together with conservation laws, like (22) and (23), as in the classical theory. As we have made explicit, developing a theory of entropy production from (20) inherently assumes that the correlations among the subsystems of a large isolated system are negligible *for all times*, and using (22) in this theory takes for granted that an appropriate mechanical description of the microscopics of heat currents has been univocally achieved.

We now propose a way to derive an entropy balance equation for the subsystems of a general isolated system from first principles, starting from the Liouville–von Neumann equation for the density matrix of the isolated system, which does not rely on the above assumptions.

IV. MASTER EQUATION FOR THE THERMODYNAMIC ENTROPY OPERATOR

We generalize the thermodynamic description to include subsystems which are not distinguished by spatial boundaries and which are not necessarily macroscopic at the atomic scale. The key point to borrow from thermodynamics is the existence of the *thermodynamic basis* $\{|\alpha\rangle\}$ and the interpretation of thermodynamic observables as those which are diagonal in this basis. That is, we consider an isolated quantum system (containing possible reservoirs) which has a Hamiltonian \hat{H} representing the energy of uncoupled subsystems, as before, and study the dynamics when the perturbation \hat{V} mixing the degrees of freedom of the different subsystems or a set of them is turned on.

The Hamiltonian of the total system is then given by $\hat{H} = \hat{H} + \hat{V}$, and the situations of interest include phenomena such as quantum quenches [13–17] or the response to applied fields [42,43,64]. After preparation of the system in an initial statistical state of the form

$$\hat{\rho}_0 = \exp(-\hat{S}_0), \quad (26)$$

with \hat{S}_0 being an arbitrary (in general unbounded) Hermitian operator with $[\hat{S}_0, \hat{V}] \neq 0$, the nonequilibrium state is described by the evolved density matrix $\hat{\rho}_t$, and we define the entropy operator \hat{S}_t by

$$\hat{\rho}_t = \exp(-\hat{S}_t) \quad \text{or} \quad \hat{S}_t = -\ln \hat{\rho}_t, \quad (27)$$

which can always be written since the density matrix is positive definite. This exponential representation of the density matrix is not new; it is a generalized form [43,70] of the nonequilibrium statistical operator introduced by Zubarev [32,33] and obtained for the case of steady states by Hershfield [71].

As discussed in the previous section, our thermodynamic entropy operator, $\hat{S}_t = -D \ln \hat{\rho}_t$, is obtained from \hat{S}_t by projecting to the space of operators diagonal in the basis $\{|\alpha\rangle\}$ of eigenstates of \hat{H} . We now establish the second law of thermodynamics for nonequilibrium transformations of the total system. For this, we consider for simplicity the specific situation of initial states diagonal in the thermodynamic basis, e.g., those of local equilibrium form as in Eq. (8), for which

$\hat{S}_0 \sim 0$ or $\hat{S}_0 = \hat{S}_0$. These initial states are usually assumed in practice [31,64,71], e.g., in transport problems.

Let us denote the diagonal (or thermodynamic) part of the density matrix of the system as

$$\hat{\varrho}_t = D \hat{\rho}_t. \quad (28)$$

The occupation probability of the state $|\alpha\rangle$ is obtained by taking matrix elements $P_{\alpha;t} = \langle \alpha | \hat{\varrho}_t | \alpha \rangle$. The proof now follows in steps by first using a corollary to Klein’s inequality [72] which states that for any *concave* function $f(x)$ we have

$$\text{Tr} f(\hat{\varrho}_t) \geq \text{Tr} f(\hat{\rho}_t). \quad (29)$$

By choosing the concave function $f(x) = -x \ln(x)$, we easily get

$$-\text{Tr} \hat{\varrho}_t \ln(\hat{\varrho}_t) \geq -\text{Tr} \hat{\rho}_t \ln \hat{\rho}_t \quad \text{or} \quad S_{d;t} \geq S_{vN;t}, \quad (30)$$

where we have denoted $S_{d;t} = -\sum_{\alpha} P_{\alpha;t} \ln P_{\alpha;t}$ as the diagonal entropy [13,35,73,74] and $S_{vN;t}$ is the well-known von Neumann entropy. Using the time invariance of $S_{vN;t}$ under the unitary evolution of the isolated system together with the fact that the initial state is diagonal, so that $S_{d;0} = S_{vN;0}$, (30) implies [13,35]

$$S_{d;t} \geq S_{d;0}. \quad (31)$$

We use this result and the Husimi-Mori lemma [30,75], which states that for any *convex* function $g(x)$ and state $|\psi\rangle$ we have

$$\langle \psi | g(\hat{\rho}_t) | \psi \rangle \geq g(\langle \psi | \hat{\rho}_t | \psi \rangle), \quad (32)$$

to show that, if we choose the convex function $g(x) = -\ln(x)$ so that $-\langle \alpha | \ln \hat{\rho}_t | \alpha \rangle \geq -\ln P_{\alpha;t}$, the thermodynamic entropy satisfies

$$S_t = \langle \hat{S}_t \rangle = -\sum_{\alpha} P_{\alpha;t} \langle \alpha | \ln \hat{\rho}_t | \alpha \rangle \geq S_{d;t} \geq S_0, \quad (33)$$

where $S_0 = S_{d;0} = S_{vN;0}$ by the assumption of the initial diagonal state. For our isolated system for which there is no entropy to be transported outside of its boundaries, this proves that S_t satisfies the second law of thermodynamics.

Note that, by splitting $\hat{\rho}_t = \hat{\varrho}_t + \hat{\rho}_t^{\sim}$ and using the convenient resolvent representation of the logarithm of an operator sum [70]

$$\ln(\hat{A} + \hat{B}) = \int_0^{\infty} dx \left(\frac{1}{x+1} - \frac{1}{x+\hat{A}+\hat{B}} \right), \quad (34)$$

we can expand the thermodynamic entropy as

$$\begin{aligned} S_t &= S_{d;t} \\ &+ \sum_{\alpha, \beta (\neq \alpha)} \left[\frac{1}{(P_{\beta;t} - P_{\alpha;t})} - \frac{P_{\alpha;t}}{(P_{\beta;t} - P_{\alpha;t})^2} \ln \frac{P_{\beta;t}}{P_{\alpha;t}} \right] \\ &\times |\langle \alpha | \hat{\rho}_t^{\sim} | \beta \rangle|^2 + O(\langle \hat{\rho}_t^{\sim} \rangle^3), \end{aligned} \quad (35)$$

with $S_t - S_{d;t} \geq 0$ due to (33); therefore, the thermodynamic entropy, unlike the diagonal entropy, is able to capture entropy-increasing processes due to quantum correlations or entanglement among the different subsystems that are encapsulated in the off-diagonal elements of the density matrix. When these quantum correlations are negligible, which, as discussed in Sec. III, is the case when each subsystem is macroscopic, the diagonal entropy *becomes* the thermodynamic entropy

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according to (35), and due to the quasistatic (or slow) nature of the global transformations involved in this case, the thermodynamic basis may be referred to as the adiabatic basis. [13,76]

The thermodynamic entropy, unlike the diagonal and von Neumann entropies, satisfies the third law of thermodynamics in a transparent way. The third law states that the thermodynamic entropy at zero temperature must be zero. The standard argument is that at zero temperature any physical state is *pure*. For an arbitrary pure state $|\psi\rangle$, there is always an orthonormal basis of Hilbert space which has this state as one of its elements (construct it via the Gram-Schmidt procedure starting from $|\psi\rangle$). Denote this basis $\{|\psi_r\rangle\}$, and order its elements such that $|\psi\rangle = |\psi_1\rangle$. We take this basis as the reference for “diagonal.” With this we then have for the diagonal and von Neumann entropies

$$\begin{aligned} S_d(\psi) &= S_{vN}(\psi) = -\sum_r P_r \ln P_r, \\ &= -1 \ln(1) - \sum_{r \neq 1} 0 \ln(0), \end{aligned} \quad (36)$$

where P_r is the probability that the system is found in state $|\psi_r\rangle$. Equation (36) is usually *understood* to be zero [72], although it is clearly an undetermined quantity since, taken at face value, $-0 \ln(0) = 0 \infty$.

The thermodynamic entropy of pure states is well defined and readily vanishes. In order to show this, we denote the density matrices (projectors) $\hat{\rho}_r = |\psi_r\rangle\langle\psi_r|$, with $\sum_r \hat{\rho}_r = \hat{1}$. We can then write

$$\ln \hat{\rho}_1 = \ln \left(\hat{1} - \sum_{r \neq 1} \hat{\rho}_r \right) = -\sum_{u=1}^{\infty} \left(\sum_{r \neq 1} \hat{\rho}_r \right)^u u^{-1}. \quad (37)$$

Using this, we can compute the thermodynamic entropy of the state $|\psi\rangle$ as

$$\mathcal{S}(\psi) = -\sum_r \langle \psi_r | \hat{\rho}_1 \mathcal{D} \ln(\hat{\rho}_1) | \psi_r \rangle = -\langle \psi | \ln(\hat{\rho}_1) | \psi \rangle. \quad (38)$$

This clearly vanishes exactly since $|\psi\rangle = |\psi_1\rangle$ is orthogonal to all $|\psi_{r \neq 1}\rangle$ involved in the last equality of (37). This establishes the third law of thermodynamics.

We are after an entropy balance equation for the subsystems, so we need an equation of motion for $\hat{\mathcal{S}}_t$ and a procedure to get from this one for each subsystem, as in the previous section. This can be obtained by first noting that the usual unitary evolution of the density matrix implies that $\hat{\mathcal{S}}_t$ also satisfies the Liouville–von Neumann equation [70] satisfied by $\hat{\rho}_t$. We have

$$i \partial_t \hat{\mathcal{S}}_t = [\hat{H}, \hat{\mathcal{S}}_t] \equiv L \hat{\mathcal{S}}_t. \quad (39)$$

This allows us to follow exactly the same procedure originally used with the density matrix [48,49] to derive an equation of motion for its diagonal part $\hat{\mathcal{Q}}_t$, the so-called Nakajima-Zwanzig generalized master equation. That is, we split the entropy operator into diagonal and nondiagonal parts, with respect to the eigenbasis of \hat{H} , as $\hat{\mathcal{S}}_t = \hat{\mathcal{S}}_t + \hat{\mathcal{S}}_t^{\sim}$ and obtain an equation of motion for the diagonal part using Zwanzig’s

integral [49]

$$i \partial_t \hat{\mathcal{S}}_t = \mathcal{D}L \hat{\mathcal{S}}_t + \mathcal{D}L e^{-itNL} \hat{\mathcal{S}}_0^{\sim} - i \int_0^t d\tau K_\tau \hat{\mathcal{S}}_{t-\tau}, \quad (40)$$

where the memory kernel is defined as [77]

$$K_\tau = \mathcal{D}L e^{-i\tau NL} \mathcal{N}L. \quad (41)$$

Now, it is easy to verify that $\mathcal{D}L\mathcal{D} = 0$ for any Hamiltonian [77]; therefore, the first term in Eq. (40) vanishes, and with our initial diagonal states implying $\hat{\mathcal{S}}_0^{\sim} = 0$, we are left with the integro-differential equation

$$\partial_t \hat{\mathcal{S}}_t = - \int_0^t d\tau K_\tau \hat{\mathcal{S}}_{t-\tau}. \quad (42)$$

Although an exact solution for (42), as well as for the similar equation satisfied by $\hat{\mathcal{Q}}_t$, can easily be found by a Laplace transformation followed by an inversion,

$$\hat{\mathcal{S}}_t = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} ds \frac{e^{st}}{s + K_s} \hat{\mathcal{S}}_0, \quad c > 0, \quad (43)$$

where K_s is the Laplace transform of the memory kernel, obtained from (41) as

$$K_s = \mathcal{D}L \frac{1}{s + iNL} \mathcal{N}L, \quad (44)$$

we restrict ourselves here, for the sake of a clear presentation and for comparison with the classical results, to the Born-Markov approximation for *weakly* coupled subsystems, leaving a more general discussion for another publication. This approximation, which is justified in the limit of very weak coupling potentials \hat{V} and very long times (Van Hove limit [78,79]), amounts to neglecting memory effects in Eq (42). In practice, this works for times *after* any transient effect or prethermalization plateau [80–82] of the isolated system has passed. We then have in this limit

$$\partial_t \hat{\mathcal{S}}_t = - \lim_{s \rightarrow 0^+} K_s \hat{\mathcal{S}}_t, \quad (45)$$

where K_s and $\hat{\mathcal{S}}_t$, after being expanded in powers of \hat{V} , are truncated up to the lowest orders, for which the well-known identity for the resolvent operator expansion

$$(A + B)^{-1} = A^{-1} - A^{-1} B (A + B)^{-1} \quad (46)$$

is very useful. Taking the expectation value of (45) and noting that for a diagonal operator $\hat{\mathcal{G}}$ we have $\langle \hat{\mathcal{G}} \rangle_t = \text{Tr} \hat{\rho}_t \hat{\mathcal{G}} = \text{Tr} \hat{\mathcal{Q}}_t \hat{\mathcal{G}}$, the average rate of change of the thermodynamic entropy in the Born-Markov limit is then

$$\langle \partial_t \hat{\mathcal{S}}_t \rangle = \sum_{\alpha\alpha'} P_\alpha W_{\alpha\alpha'} \ln \frac{P_\alpha}{P_{\alpha'}}, \quad (47)$$

with the transition rates $W_{\alpha\alpha'} = 2\pi \delta(\varepsilon_\alpha - \varepsilon_{\alpha'}) |V_{\alpha\alpha'}|^2$, calculated in the lowest order in the coupling potential using Fermi’s golden rule. Here, we have derived the transition rates from (44) and (45) by using the representation of the δ function [83]

$$\lim_{s \rightarrow 0^+} \text{Re} \frac{1}{s + i\omega} = \pi \delta(\omega). \quad (48)$$

Moreover, $P_\alpha = \langle \alpha | \hat{\mathcal{Q}}_t^{(0)} | \alpha \rangle$ is the occupation probability of the state $|\alpha\rangle$ in its lowest-order approximation [48], which

also satisfies the Born-Markov limit of the generalized master equation, that is, the transport (or Pauli) equation

$$\partial_t P_\alpha = \sum_{\alpha'} (P_{\alpha'} W_{\alpha'\alpha} - P_\alpha W_{\alpha\alpha'}). \quad (49)$$

The right-hand side of (47) can be rearranged to yield the quantum version, in the Born-Markov limit, of the entropy balance equation. We find

$$\langle \partial_t \hat{S}_t \rangle = \Pi - \Phi, \quad (50)$$

where the average rate of entropy produced in the system is interpreted as [84–88]

$$\Pi = \frac{1}{2} \sum_{\alpha, \alpha'} (P_\alpha W_{\alpha\alpha'} - P_{\alpha'} W_{\alpha'\alpha}) \ln \frac{P_\alpha W_{\alpha\alpha'}}{P_{\alpha'} W_{\alpha'\alpha}} \quad (51)$$

and the average entropy flux toward the surroundings is interpreted as

$$\Phi = \frac{1}{2} \sum_{\alpha, \alpha'} (P_\alpha W_{\alpha\alpha'} - P_{\alpha'} W_{\alpha'\alpha}) \ln \frac{W_{\alpha\alpha'}}{W_{\alpha'\alpha}}. \quad (52)$$

Of course, the latter must be zero for an isolated system since a global entropy current finds nowhere to go in this case. The vanishing of this quantity is clearly seen from the symmetry of the transition rates $W_{\alpha\alpha'}$ under the interchange of indices, resulting from the Hermiticity of the perturbation \hat{V} . A nonvanishing entropy current is obtained, however, when we consider the local entropy production in a subsystem of a larger system, as in the electrical conduction problem of Sec. VI.

Note that Π is a sum of terms of the form $(x - y) \ln(x/y)$, so it is always *non-negative*. Furthermore, it vanishes for reversible transformations (local equilibrium) or in equilibrium due to detailed balance, $P_\alpha^r W_{\alpha\alpha'} = P_{\alpha'}^r W_{\alpha'\alpha}$, which is a statistical statement of the second law of thermodynamics in the Clausius form. The outlined method is the one that we shall follow in Sec. VI for the electrical conduction problem to derive an entropy balance equation for the electronic subsystem in the Born-Markov limit based on the transport equation for the total electrons + phonons + field system, without any need to invoke expressions like (20) together with extra conservation laws.

One of the advantages of our approach, besides being grounded in fundamental facts regarding the nature of thermodynamic observables, is that, as opposed to actively studied relative-entropy formulations [37–39] of quantum entropy production, it can be generalized to initial states with correlations among the subsystems, i.e., not of the local equilibrium form. This is very important since neglecting correlations in the state of an isolated system is inconsistent with the specification of its energy [89]. We have safely ignored this fact in our present discussion because the consideration of a nonvanishing second term in Eq. (40), due to $\hat{S}_0^\sim \neq 0$, only adds the term

$$\frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} ds \frac{e^{st}}{s + K_s} \mathcal{D}L \frac{1}{s + i\mathcal{N}L} \hat{S}_0^\sim \quad (53)$$

to the solution (43). However, it is easily seen that expressions containing \hat{S}_0^\sim contribute higher-order terms in the weak-coupling expansion embodied in the Born-Markov limit and

then are negligible; the same happens [48] for the contributions coming from $\hat{\rho}_0^\sim$ in the Born-Markov limit of the generalized master equation for $\hat{\rho}_t$. Therefore, our formalism has room to study memory effects and strong correlations in the initial state by only straightforward modifications. These memory effects are the ones responsible for heat transport depending on the path of thermodynamic states in phenomenological thermodynamics.

V. RELATION WITH CLASSICAL STOCHASTIC THERMODYNAMICS

We now show that our result, (47), is consistent with the result for the average rate of change of the thermodynamic entropy obtained in Onsager’s classical theory. We consider an isolated macroscopic system which has been left alone for a very long time (aged system). The classical thermodynamic state is described by a set of extensive variables, such as energy, mass, electric charge, etc., which randomly fluctuate about their equilibrium values and whose values define the classical state of the system. This state is represented by the symbol \mathbf{a}_t (shifted to vanish in equilibrium), whose successive values in time describe a stationary stochastic process.

It can be shown that, if the fluctuations follow a Gaussian process, which can be argued to be the case if the extensive variables are algebraic sums of very many independent (weakly coupled) “microscopic” quantities so that the central limit theorem can be invoked, and if in addition the process is Markovian, then the joint probability distribution,

$$\Omega(\mathbf{a}', \Delta t, \mathbf{a}'') = P_{\mathbf{a}'} P_{\mathbf{a}''}(\Delta t), \quad (54)$$

for observing the values $\mathbf{a}_{t'} = \mathbf{a}'$ and $\mathbf{a}_{t''} = \mathbf{a}''$ at the respective times separated by an interval $\Delta t = t'' - t'$, with $P_{\mathbf{a}'\mathbf{a}''}(\Delta t)$ being the corresponding conditional probability to make a transition between these states, is given by Onsager’s principle [90–92], which we write as [93]

$$2 \ln \Omega(\mathbf{a}', \Delta t, \mathbf{a}'') = \mathcal{S}_{\mathbf{a}'} + \mathcal{S}_{\mathbf{a}''} + \left(\int_{t'}^{t''} d\tau \dot{S} \right)_{\min}, \quad (55)$$

where the path of integration is the trajectory \mathbf{a}_τ , which makes the integral a minimum, subject to the conditions $\mathbf{a}_{t'} = \mathbf{a}'$ and $\mathbf{a}_{t''} = \mathbf{a}''$. Clearly, if we take the limit $\Delta t \rightarrow 0$, the integral tends to $\dot{S}_{\mathbf{a}'} \Delta t$, where $\dot{S}_{\mathbf{a}'}$ is the entropy production rate in the state \mathbf{a}' , whose entropy is related to the probability distribution $P_{\mathbf{a}'}$ by Boltzmann’s principle. Subtracting the time-reversed expression of Onsager’s principle from (55), we get, in the limit $\Delta t \rightarrow 0$, the alternative form

$$\ln \frac{\Omega(\mathbf{a}', \Delta t, \mathbf{a}'')}{\Omega(\mathbf{a}'', -\Delta t, \mathbf{a}')} = \frac{1}{2} (\dot{S}_{\mathbf{a}'} + \dot{S}_{\mathbf{a}''}) \Delta t. \quad (56)$$

We now average (56) over the joint distribution (54), which is expanded up to linear order in Δt by writing the transition probabilities to go from \mathbf{a}' to \mathbf{a}'' after a time Δt as

$$P_{\mathbf{a}'\mathbf{a}''}(\Delta t) = \delta_{\mathbf{a}'\mathbf{a}''} + W_{\mathbf{a}'\mathbf{a}''} \Delta t = P_{\mathbf{a}'\mathbf{a}''}(-\Delta t), \quad (57)$$

with the last equality being the statement of Onsager’s microscopic reversibility [90,94] and leading to the symmetry of the transition rates $W_{\mathbf{a}'\mathbf{a}''}$ under the interchange of indices. This symmetry allows us to write the averaged left-hand side of (56) as $\Delta t \sum_{\mathbf{a}'\mathbf{a}''} P_{\mathbf{a}'} W_{\mathbf{a}'\mathbf{a}''} \ln(P_{\mathbf{a}'}/P_{\mathbf{a}''})$ and the right-hand side

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as $\Delta t \sum_{a'} P_{a'} \dot{S}_{a'}$. Therefore, by recognizing the latter sum as $\langle \dot{S} \rangle$, we get the expression

$$\langle \dot{S} \rangle = \sum_{a'a''} P_{a'} W_{a'a''} \ln \frac{P_{a'}}{P_{a''}}, \quad (58)$$

which gives the desired link with our theory by making a comparison with (47). We remark that (56) is of the same form [5],

$$\ln \frac{P_{\Delta t}(\sigma)}{P_{\Delta t}(-\sigma)} = \sigma \Delta t, \quad (59)$$

as Gallavotti and Cohen's fluctuation theorem [95] if we read $(1/2)(\dot{S}_{a'} + \dot{S}_{a''})$ as a realization of the random number $\sigma = (1/2)(\dot{S}_{a'} + \dot{S}_{a''})$, representing the average entropy production in going from a' to a'' during a time interval Δt along the stochastic trajectory of states, and translate the joint probability $\Omega(a', \pm \Delta t, a'')$ to have the state realizations $a' = a'$ and $a'' = a''$ in a forward ($+\Delta t$) or backward ($-\Delta t$) evolution to the corresponding probabilities $P_{\Delta t}(\pm \sigma)$ to have the realization $(1/2)(\dot{S}_{a'} + \dot{S}_{a''})$ of σ or its time-reversed value.

VI. ENTROPY PRODUCTION IN ELECTRICAL CONDUCTION

We next apply the formalism to a model of independent electrons coupled to phonons in the presence of an electric field. We are interested in the average rate of entropy produced in the electronic system and transported to the phonons in the steady state. The picture is then that of a large system divided into three subsystems, the electrons, the phonons, and the sources of the field. In the thermodynamic description we parametrize, as usual, the coupling to the latter by introducing E_t and forgetting about the structure of this subsystem.

The Hamiltonian of the total system is then

$$\hat{H} = \hat{H}_{\text{el}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{el-ph}} + \hat{H}_{F;t}, \quad (60)$$

where $\hat{H}_{\text{el}} = \sum_k \epsilon_k \hat{c}_k^\dagger \hat{c}_k$ is the kinetic-energy operator for the electrons, which are assumed to be free except for their interaction with the field and the phonons, the energy operator of the phonon subsystem is $\hat{H}_{\text{ph}} = \sum_q \omega_q \hat{a}_q^\dagger \hat{a}_q$, and the electron-phonon interaction is bilinear in electron operators and linear in phonon operators,

$$\hat{H}_{\text{el-ph}} = \sum_{qkk'} M_{kk'}^q \hat{c}_k^\dagger \hat{c}_k (\hat{a}_q + \hat{a}_{-q}^\dagger), \quad (61)$$

with $M_{kk'}^q$ representing the strength of the coupling. The generalization to multiple electronic bands and multiple phonon branches is straightforward and does not change the results. Finally, $\hat{H}_{F;t}$ represents the effects of the applied electric field E_t and can be written in first-quantized notation as $\hat{H}_{F;t} = -e E_t \cdot \sum_e \hat{x}_e$, where \hat{x}_e is the displacement of electron e from some arbitrarily chosen reference position.

Up to time $t = 0$ we have a collection of electrons in local equilibrium with the lattice vibrations of a metal at a temperature T and no applied electric field, i.e., $E_0 = 0$. The initial state is then of the form

$$\hat{\rho}_0 = Z^{-1} \exp[-(\hat{H}_0 - \mu \hat{N}_{\text{el}})/T], \quad (62)$$

where $Z = Z_{\text{el}} Z_{\text{ph}}$ is the grand-partition function, \hat{N}_{el} is the operator for the total number of electrons, and \hat{H}_0 is the Hamiltonian of the uncoupled subsystems,

$$\hat{H}_0 = \hat{H}_{\text{el}} + \hat{H}_{\text{ph}}, \quad (63)$$

whose eigenstates, constituting the thermodynamic basis, are

$$|\alpha\rangle = |n_1 n_2 \cdots n_k \cdots\rangle |N_1 N_2 \cdots N_q \cdots\rangle = |n; N\rangle, \quad (64)$$

which represent the numbers of electrons, $\{n_k\}$, and phonons, $\{N_q\}$, in each single-particle state.

The electric field is turned on at time $t = 0^+$ to a constant value, i.e., $E_t = E$ for $t > 0$, and the subsystems are subsequently coupled. In the notation of Sec. IV we then have in the generalized thermodynamic description

$$\hat{H} = \hat{H}_0 + \hat{H}_F, \quad \hat{V} = \hat{H}_{\text{el-ph}}. \quad (65)$$

Note that \hat{V} is the coupling which fully mixes the degrees of freedom of the different subsystems (like \hat{H}_{lm} in Sec. III), which need not be separated by spatial boundaries. We now explain with some detail how the perturbation scheme developed in Sec. IV applies to the present case. However, we only need to concentrate on how the transport equation is obtained in the Born-Markov limit since this suffices to get the average rate of entropy production.

The idea is then to first derive the transport equation for the total system from the Liouville-von Neumann equation; we do it much in the same spirit as Kohn and Luttinger [96] did for elastic electronic scattering, generalized by Argyres [97] to inelastic scattering. Having this transport equation, the average rate of change of the total thermodynamic entropy in the Born-Markov limit is

$$\langle \partial_t \hat{S}_t \rangle = - \sum_{\alpha} (\partial_t P_{\alpha}) \ln P_{\alpha}, \quad (66)$$

as can easily be verified by using (49) in Eq. (47). By proceeding with the transport or quantum Boltzmann equation for the electronic subsystem, we obtain a simple expression for the electronic entropy production.

For the purpose of the present discussion, it suffices to work with the Liouville-von Neumann equation to first order in the electric field. That is, with $\hat{\rho}_t = \hat{\rho}_0 + \hat{\rho}_{1;t}$ and $\hat{\rho}_{1;t}$ linear in the electric field, we write

$$i \partial_t \hat{\rho}_{1;t} = [\hat{H}_0 + \hat{V}, \hat{\rho}_{1;t}] + [\hat{H}_F, \hat{\rho}_0], \quad (67)$$

where $\hat{\rho}_{1;0} = 0$. The Laplace transform of this equation, with $\hat{\rho}_{1;s} = \int_0^{\infty} e^{-st} \hat{\rho}_{1;t}$, reads

$$is \hat{\rho}_{1;s} = (\mathcal{L}_0 + L_V) \hat{\rho}_{1;s} + s^{-1} L_F \hat{\rho}_0. \quad (68)$$

With $\hat{\rho}_{1;s} = \mathcal{D} \hat{\rho}_{1;s}$ and $\hat{\rho}_{1;s}^{\sim} = \mathcal{N} \hat{\rho}_{1;s}$, we separate this equation into diagonal and nondiagonal parts, obtaining, respectively, the coupled algebraic equations

$$is \hat{\rho}_{1;s} = \mathcal{D} L_V \hat{\rho}_{1;s}^{\sim} + s^{-1} \mathcal{D} L_F \hat{\rho}_0, \quad (69)$$

$$[is + \mathcal{N}(\mathcal{L}_0 + L_V)] \hat{\rho}_{1;s}^{\sim} = \mathcal{N} L_V \hat{\rho}_{1;s} + s^{-1} \mathcal{N} L_F \hat{\rho}_0. \quad (70)$$

Solving for $\hat{\rho}_{1;s}^{\sim}$ in Eq. (70) and substituting the result in Eq. (69), we get a decoupled equation for $\hat{\rho}_{1;s}$, which in the

lowest Born approximation for the electron-phonon scattering reads

$$is\hat{\rho}_{1;s} = \mathcal{D}L_V \frac{1}{is + \mathcal{N}\mathcal{L}_0} \mathcal{N}L_V \hat{\rho}_{1;s} + s^{-1} \mathcal{D}L_F \hat{\rho}_0. \quad (71)$$

From this, the transport equation for the total system easily arises in the Born-Markov limit by taking the Laplace inverse and neglecting memory terms. In terms of the occupation probabilities $P_\alpha = \langle \alpha | \hat{\rho}_t | \alpha \rangle$ we get

$$\partial_t P_\alpha = \frac{1}{i} (L_F \hat{\rho}_0)_\alpha + \sum_{\alpha'} (P_{\alpha'} W_{\alpha'\alpha} - P_\alpha W_{\alpha\alpha'}) \quad (72)$$

with the transition rates induced by the electron-phonon coupling $W_{\alpha\alpha'} = 2\pi \delta(\varepsilon_\alpha - \varepsilon_{\alpha'}) |\langle \alpha | \hat{H}_{\text{el-ph}} | \alpha' \rangle|^2$. We have then derived the transport equation for the total system, in terms of which the average rate of change of the total thermodynamic entropy can be calculated, in the Born-Markov limit using (66).

To proceed with the calculation of the entropy production of the electronic subsystem, we note that

$$P_\alpha = P_n^{\text{el}} P_N^{\text{ph}} \chi_{nN}^{\text{el-ph}}, \quad (73)$$

where P_n^{el} is the probability that the electrons are in the Fock state $|n\rangle$ regardless of the state of the phonons, P_N^{ph} is the probability that the phonons are in the Fock state $|N\rangle$ regardless of the state of the electrons, and $\chi_{nN}^{\text{el-ph}}$ is the conditional probability that the total system is in the state $|\alpha\rangle$ in Eq. (64), given that the electron and phonon subsystems are in states $|n\rangle$ and $|N\rangle$, respectively, without “knowing” about each other. Clearly, $\chi_{nN}^{\text{el-ph}}$ is a function of the electron-phonon coupling strength and can then be expanded in a power series of it,

$$\chi_{nN}^{\text{el-ph}} = 1 + \chi_{nN}^{\text{el-ph(1)}} + \chi_{nN}^{\text{el-ph(2)}} + \dots \quad (74)$$

In the lowest Born approximation for the electron-phonon scattering, the electron and phonon subsystems are uncorrelated, i.e., $\chi_{nN}^{\text{el-ph}} = 1$, which is the usual Born-Oppenheimer approximation, and then by substituting (72) and (73) into (66), the average rate of change of the thermodynamic entropy of the total system turns out to be additive. For the electronic subsystem we have

$$\langle \partial_t \hat{S}_t \rangle_{\text{el}} = - \sum_n (\partial_t P_n^{\text{el}}) \ln P_n^{\text{el}}, \quad (75)$$

where the normalization condition $\sum_N P_N^{\text{ph}} = 1$ has been used. Here, the transport equation for the electronic subsystem is obtained from (72) by summing over N ,

$$\partial_t P_n^{\text{el}} = \frac{1}{i} \sum_N (L_F \hat{\rho}_0)_{nN,nN} + \sum_{n'} (P_{n'}^{\text{el}} \Gamma_{n'n} - P_n^{\text{el}} \Gamma_{nn'}), \quad (76)$$

where we have defined the phonon-averaged reduced transition rates $\Gamma_{nn'}$ as

$$\Gamma_{nn'} = \sum_N P_N^{\text{ph}} \sum_{N'} W_{nN,n'N'}. \quad (77)$$

We can still go further and use the assumed statistical independence of the electrons to factorize their probability distribution into the probabilities of the one-electron states

$$P_n^{\text{el}} = p_{n_1} p_{n_2} \dots p_{n_k} \dots, \quad (78)$$

where p_{n_k} is the probability that the one-electron state with quantum number k has occupation $n_k = 0, 1$. Substituting this in Eq. (75), we obtain an additive contribution to the average rate of change of the thermodynamic entropy of the electronic subsystem

$$\langle \partial_t \hat{S}_t \rangle_{\text{el}} = - \sum_{k,n_k} (\partial_t p_{n_k}) \ln p_{n_k} = - \sum_k (\partial_t f_k) \ln \frac{f_k}{1-f_k}, \quad (79)$$

where in the last equality we identify the nonequilibrium one-electron distribution as $f_k = \sum_{n_k} n_k p_{n_k} = p_{n_k=1}$ and use $\sum_{n_k} p_{n_k} = 1$ to express $p_{n_k=0} = 1 - f_k$. The transport equation for f_k is obtained by multiplying (76) by n_k and summing over all n . To this end, note that

$$\Gamma_{nn'} = \sum_{k,k'(k \neq k')} w_{kk'} n_k (1 - n_{k'}) \times |\langle \dots n_{k'} - 1 \dots n_k + 1 \dots n' \rangle|^2, \quad (80)$$

which is obtained by using (61) explicitly, where the one-electron transition rate from state k to state k' is

$$w_{kk'} = 2\pi \sum_q |M_{k'k}^q|^2 [\bar{N}(\omega_q) \delta(\varepsilon_{k'} - \varepsilon_k - \omega_q) + [1 + \bar{N}(\omega_q)] \delta(\varepsilon_k - \varepsilon_{k'} + \omega_q)], \quad (81)$$

with $\bar{N}(\omega_q) = \sum_N P_N^{\text{ph}} \langle N | \hat{a}_q^\dagger \hat{a}_q | N \rangle$ being the average number of phonons in the single-particle state with quantum number q . We assume that the phonon subsystem can be kept in equilibrium at temperature T (hence the dependence of \bar{N} on only ω_q), regardless of the nonequilibrium state of the electrons, as is the case for a good-enough heat reservoir.

That the phonons can be considered as a heat reservoir in the Born-Oppenheimer approximation can be seen by looking at the transport equation for the phonon subsystem, obtained from (72) by summing over n ,

$$\partial_t P_N^{\text{ph}} = \sum_{N'} (P_{N'}^{\text{ph}} \Theta_{N'N} - P_N^{\text{ph}} \Theta_{NN'}), \quad (82)$$

where we have defined the electron-averaged reduced transition rates as

$$\Theta_{NN'} = \sum_n P_n^{\text{el}} \sum_{n'} W_{nN,n'N'}. \quad (83)$$

Here, we observe the important fact that the contribution from the first term of (72) vanishes due to the null value of the trace of the commutator $[\hat{H}_F, \hat{\rho}_0]$ in the subspace of electrons. This allows the existence of a steady-state solution of (82) for which detailed balance holds, which is then an equilibrium solution. In any case, the assumption that the phonons are in equilibrium is not necessary for the following derivation of the electronic entropy production, as $\bar{N}(\omega_q)$ in Eq. (81) can be replaced by the more complicated average obtained by using the nonequilibrium solution of (82), not investigated here.

The transport equation for the one-electron distribution is then found to be, from (76),

$$\partial_t f_k = \frac{1}{i} \sum_{nN} n_k (L_F \hat{\rho}_0)_{nN,nN} + \sum_{n'} n_k (P_{n'}^{\text{el}} \Gamma_{n'n} - P_n^{\text{el}} \Gamma_{nn'}). \quad (84)$$

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This is just the quantum Boltzmann equation. To write it in the familiar form we first note that, by writing \hat{H}_{el} in the first-quantized form and using the well-known formula $[\hat{\mathbf{x}}_e, f(\hat{\mathbf{p}}_e)] = i\nabla_{\hat{\mathbf{p}}_e} f(\hat{\mathbf{p}}_e)$, we have $L_F \hat{\rho}_0 = i(e/T)\mathbf{E} \cdot \hat{\mathbf{v}} \hat{\rho}_0$, where $\hat{\mathbf{v}} = \sum_e (\hat{\mathbf{p}}_e/m) = \sum_k \mathbf{v}_k \hat{c}_k^\dagger \hat{c}_k$ is the velocity operator of all electrons, with $\mathbf{v}_k = \nabla_k \epsilon_k$ being the band velocity. Therefore, the first term in Eq. (84) is

$$\begin{aligned} (\partial_t f_k)_{\text{drift}} &= \frac{1}{i} \sum_{nN} n_k (L_F \hat{\rho}_0)_{nN, nN} = \frac{e\mathbf{E}}{T} \text{Tr}(\hat{n}_k \hat{\mathbf{v}} \hat{\rho}_0) \\ &= e\mathbf{E} \cdot \mathbf{v}_k f_k^0 (1 - f_k^0) / T = -e\mathbf{E} \cdot \nabla_k f_k^0, \end{aligned} \quad (85)$$

where $f_k^0 = \text{Tr}(\hat{n}_k \hat{\rho}_0)$ is the equilibrium Fermi-Dirac one-electron distribution. The second term in Eq. (84) can be written, using (80), as

$$\begin{aligned} (\partial_t f_k)_{\text{coll}} &= \sum_{nn'} n_k (P_{n'}^{\text{el}} \Gamma_{n'n} - P_n^{\text{el}} \Gamma_{nn'}), \\ &= \sum_n P_n^{\text{el}} n_k \sum_{k', k''} w_{k'k''} (1 - n_{k'}) n_{k''} \\ &\quad - \sum_n P_n^{\text{el}} n_k \sum_{k', k''} w_{k'k''} n_{k'} (1 - n_{k''}). \end{aligned} \quad (86)$$

Therefore, by noting that $n_k(1 - n_k) = 0$ and using (78), we see that the terms which do not cancel in the above sums are

$$(\partial_t f_k)_{\text{coll}} = \sum_{k'} [f_{k'} w_{k'k} (1 - f_k) - f_k w_{kk'} (1 - f_{k'})]. \quad (87)$$

We have thus arrived at the familiar form of the quantum Boltzmann equation by substituting (85) and (87) into (84). With this, we can rewrite the average rate of change of the thermodynamic entropy of the electronic subsystem, from (79), as

$$\langle \partial_t \hat{\mathcal{S}}_t \rangle_{\text{el}} = \Pi_{\text{el}} - \Phi_{\text{el}}, \quad (88)$$

which is the entropy balance equation for the electronic subsystem, with the average electronic entropy production rate

$$\begin{aligned} \Pi_{\text{el}} &= \frac{1}{2} \sum_{kk'} [f_{k'} w_{k'k} (1 - f_k) - f_k w_{kk'} (1 - f_{k'})] \\ &\quad \times \ln \frac{f_{k'} w_{k'k} (1 - f_k)}{f_k w_{kk'} (1 - f_{k'})}, \end{aligned} \quad (89)$$

which, similar to (51), is a sum of terms of the form $(x - y) \ln(x/y)$ and then satisfies the second law of thermodynamics; the entropy flux from the electrons to the phonons is

$$\begin{aligned} \Phi_{\text{el}} &= \frac{1}{2} \sum_{kk'} [f_{k'} w_{k'k} (1 - f_k) - f_k w_{kk'} (1 - f_{k'})] \ln \frac{w_{k'k}}{w_{kk'}} \\ &\quad + \sum_k (\partial_t f_k)_{\text{drift}} \ln \frac{f_k}{1 - f_k}. \end{aligned} \quad (90)$$

In the steady state the left-hand side of (88) is exactly zero, and then all the entropy produced in the electronic system is transported to the phonons. We now want to show that this steady-state entropy flux toward the lattice vibrations gives the expression of the well-known Joule heating.

We need a solution, $f_k = f_k^0 + \delta f_k$, of the quantum Boltzmann equation which, to linear order in the electric field strength, we write formally as

$$\delta f_k = \sum_{k'} \mathcal{W}_{kk'}^{-1} \left[\frac{e\mathbf{E} \cdot \mathbf{v}_{k'}}{T} f_{k'}^0 (1 - f_{k'}^0) \right], \quad (91)$$

where the linearized collision operator \mathcal{W} has matrix elements

$$\mathcal{W}_{kk'} = f_k^0 w_{kk'} + w_{k'k} (1 - f_k^0) - \frac{\delta_{kk'}}{\tau_k}. \quad (92)$$

The quasiparticle relaxation time τ_k is given by

$$\frac{1}{\tau_k} = \sum_{k'} [f_{k'}^0 w_{k'k} + w_{kk'} (1 - f_{k'}^0)] \quad (93)$$

and becomes equal to the momentum relaxation time if the transition rates $w_{kk'}$ are independent of the angle between k and k' .

We now expand (89). Because both the logarithm and the prefactor vanish in equilibrium, the leading contribution is $O(\delta f)^2$. The term from expanding the logarithm is easily seen to be

$$\frac{\delta f_{k'}}{f_{k'}^0 (1 - f_{k'}^0)} - \frac{\delta f_k}{f_k^0 (1 - f_k^0)},$$

while the term coming from the prefactor is

$$\mathcal{W}_{kk'} \delta f_{k'} - \mathcal{W}_{k'k} \delta f_k. \quad (94)$$

Combining these equations with (91) yields

$$\Pi_{\text{el}} = \sum_k \frac{e\mathbf{E} \cdot \mathbf{v}_k}{T} \delta f_k = \frac{\sigma E^2}{T}, \quad (95)$$

where, in the last equality, we recognize the electric current as $e\langle \hat{\mathbf{v}} \rangle = \sum_k e \mathbf{v}_k \delta f_k = \sigma \mathbf{E}$, with σ being the electric conductivity. Thus, we see that, to leading order in the electron-phonon coupling and the electric field and on the assumption that the phonons act as a reservoir, the electronic entropy production predicted by our formula is exactly the result expected from the Joule heating, $T\Pi_{\text{el}} = \sigma E^2$, implied by the electric field. Therefore, as desired, we have arrived at an expression of energy dissipation from a first-principles calculation of entropy production, not the other way around, as in previous approaches.

We remark that the results for the entropy production presented here are beyond the linear response theory. This is because, even when starting from the linear in the electric field correction to the density matrix $\hat{\rho}_{1,\nu}$ [see Eq. (67)], we derived the leading contribution to the electronic entropy production which is quadratic in the electric field. This is in contrast to past approaches [43,96] for the calculation of the Joule heating, which require going to the second order in the electric field contribution to the density matrix $\hat{\rho}_{2,\nu}$ for the calculation of the rate of change of the energy of the electrons. A field-theoretic approach [98,99] for the calculation of higher-order terms in the entropy production beyond the Born-Markov approximation will be treated elsewhere.

It is illustrative to evaluate the result explicitly, assuming, e.g., dispersionless optical phonons $\omega_q = \omega_0$. With $|M_{k'k}^q|^2 = M \delta_{q, k'-k}$ and assuming a degenerate electron system (i.e.,

$T \ll \epsilon_F$, we obtain

$$\Pi_{\text{el}} = \frac{(e^2 E^2 / 3\pi m M) D_{\epsilon_F}}{D_{\epsilon_F - \omega_0} + D_{\epsilon_F + \omega_0}} (\epsilon_F / T) \sinh(\omega_0 / T), \quad (96)$$

with D_ϵ being the electron density of states. In this case, the entropy production becomes large at low temperatures due to an increase in the conductivity (phonons not thermally activated and then scarcity of scattering centers) and hence in the Joule heating; this is expected when the only scattering mechanism is from optical phonons.

Finally, we would like to point out the connection of the result (95) with the discussion in Sec. III concerning the foundations of the classical theory. With only the action of one of the subsystems (the sources of the \mathbf{E} field) treated parametrically, with the three spatial components of the field E_λ playing the role of the external parameters to the electronic subsystem, we can define an operator $\hat{F}_\lambda = \partial \hat{H}_F / \partial E_\lambda$ for the force exerted on the electrons upon variation of the field and write

$$\begin{aligned} T \dot{\Pi}_{\text{el}} &= \sum_\lambda \hat{F}_\lambda \partial_t E_\lambda = \partial_t \sum_\lambda \hat{F}_\lambda E_\lambda - \sum_\lambda (\partial_t \hat{F}_\lambda) E_\lambda \\ &= \partial_t \hat{H}_F + e \dot{\mathbf{v}} \cdot \mathbf{E} = e \dot{\mathbf{v}} \cdot \mathbf{E}, \end{aligned} \quad (97)$$

where $\hat{H}_F = -e \sum_{\lambda,e} E_\lambda \hat{x}_e^\lambda$, and to get the last equality we use $\partial_t \hat{H}_F = \partial_t \hat{H} = 0$ since the total system is isolated. Taking the expectation value of (97), the last equality is just (95), and the form of the first equality is reminiscent of the classical expression (25).

We then see that, although in the present discussion the subsystems are not separated by spatial boundaries (the essence of the generalized thermodynamic description) and there is no local equilibrium at all times: the phonons remain in

equilibrium, as implied by the assumption that they constitute a good heat reservoir, but the electrons attain a nonequilibrium steady state; the common feature with the discussion in Sec. III is the complete factorization of the probability distribution of the system over the degrees of freedom of the different subsystems (uncorrelated subsystems), here manifested as the Born-Oppenheimer approximation. An appropriate account of the quantum correlations between subsystems is therefore the key to purely quantum thermodynamic behavior.

VII. CONCLUSION

We have developed a theory for the entropy production in quantum many-body systems by introducing an entropy operator and calculating the average rate of change of its thermodynamically measurable part. We show that the laws of thermodynamics are satisfied exactly within our formalism. In the Born-Markov approximation which describes the physics of weakly coupled subsystems of an isolated system in the long-time limit, the theory reproduces the entropy balance equation which is fundamental in classical nonequilibrium thermodynamics and the Joule heating contribution to the entropy production expected in a standard conductor. Applications to other systems as well as generalizations beyond the weak-coupling limit will be presented elsewhere.

ACKNOWLEDGMENTS

E.S.-C. would like to acknowledge the support from the Fulbright-Colciencias fellowship and the Columbia GSAS Faculty fellowship. The work of A.J.M. was supported by the National Science Foundation under Grant No. DMR-1308236.

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Chapter 3

Entropy Production in the One-Atom Maser

The main results of this work are published in:

E. Solano-Carrillo, Entropy production and thermalization in the one-atom maser, *Phys. Rev. E* **94**, 062116 (2016).

The actual published text is shown at the end of this chapter.

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3.1 Overview

In the configuration in which two-level atoms with an initial thermal distribution of their states are sent in succession to a cavity sustaining a single mode of electromagnetic radiation, one atom leaving the cavity as the next one enters it—as in the one-atom maser—[Jaynes and Cummings \(1963\)](#) showed that the steady state of the field, when many atoms have traversed the cavity, is thermal with a temperature different than that of the atoms in the off-resonant situation. Having an interaction between two subsystems which maintains them at different temperatures was then understood as leading to an apparent violation of energy conservation.

In this chapter we show, by calculating the quantum entropy production in the system and interpreting according to the theory developed in the previous chapter,

that this difference of temperatures is consistent with having the subsystems adiabatically insulated from each other as the steady state is approached. At resonance the insulation is removed and equilibration of the temperatures is achieved. This solves the puzzle which was originally left unexplained by Jaynes and Cummings.

In order to make the exposition as complete as possible we organize the work as follows. In section 3.2 we give a brief background of the Jaynes-Cummings model and the features which are relevant for our discussion. In section 3.4 we discuss the aforementioned configuration of the one-atom maser, including the derivation of the Jaynes-Cummings formula for the steady-state temperature of the field in term of that of the atoms. An original proof of the fact that every atom just entering the cavity “sees” a *thermal* distribution of photons in the cavity is also given in this section. In section 3.5 we calculate the entropy production in the Jaynes-Cummings thought experiment, show how it tends to its steady state value and compare it with expectations from classical nonequilibrium thermodynamics. We conclude with section 3.6.

3.2 Background

3.2.1 Jaynes-Cummings model

The Jaynes-Cummings model describes the electric dipole coupling of a quantized single mode (energy ω) of electromagnetic radiation in a cavity, with a two-level atom with energy splitting $\Omega = E_2 - E_1$. The Hamiltonian describing the cavity field + atom system is, in the rotating wave approximation,

$$\hat{H} = E_1 \hat{\pi} \hat{\pi}^\dagger + E_2 \hat{\pi}^\dagger \hat{\pi} + \omega \hat{a}^\dagger \hat{a} + \gamma (\hat{\pi}^\dagger \hat{a} + \hat{\pi} \hat{a}^\dagger), \quad (3.1)$$

where \hat{a}^\dagger (\hat{a}) is the creation (annihilation) operator of a photon in the cavity, $\hat{\pi}^\dagger$ and $\hat{\pi}$ are the ladder operators for the atomic states and γ is the strength of the dipole coupling, assumed small (see section 3.4.1):

$$\gamma \ll \Omega. \quad (3.2)$$

We work in the natural basis $\{|\alpha\rangle\} = \{|1, n+1\rangle, |2, n\rangle\}$ which diagonalizes the Hamiltonian of *uncoupled* subsystems $\hat{\mathcal{H}} = E_1 \hat{\pi} \hat{\pi}^\dagger + E_2 \hat{\pi}^\dagger \hat{\pi} + \omega \hat{a}^\dagger \hat{a}$, where $\{|1\rangle, |2\rangle\}$ are the two states of the atom (ground & excited), with

$$\hat{\pi}^\dagger |1\rangle = |2\rangle, \quad \hat{\pi}^\dagger |2\rangle = 0, \quad \hat{\pi} |2\rangle = |1\rangle, \quad \hat{\pi} |1\rangle = 0, \quad (3.3)$$

and n is the number of photons in the cavity. In the sector with n photons, the matrix representation H_n of the total Hamiltonian then reads

$$H_n = \begin{pmatrix} E_1 + (n+1)\omega & \gamma\sqrt{n+1} \\ \gamma\sqrt{n+1} & E_2 + n\omega \end{pmatrix}, \quad (3.4)$$

with $H = \bigoplus_n H_n$. Defining the atomic zero of energy so that $E_1 + E_2 = 0$, we get for the eigenvalues of H_n

$$E_n^\pm = (n+1/2)\omega \pm \beta_n, \quad (3.5)$$

with $2\beta_n = \sqrt{(\Omega - \omega)^2 + 4(n+1)\gamma^2}$ and the corresponding eigenvectors

$$\begin{aligned} |\phi_n^+\rangle &= \cos \theta_n |2, n\rangle + \sin \theta_n |1, n+1\rangle, \\ |\phi_n^-\rangle &= -\sin \theta_n |2, n\rangle + \cos \theta_n |1, n+1\rangle, \end{aligned} \quad (3.6)$$

with θ_n indicating the angle of rotation of the basis vectors defining the n -photon sector, where

$$\tan(2\theta_n) = \frac{2\gamma\sqrt{n+1}}{\Omega - \omega}. \quad (3.7)$$

Inverting (3.6) and noting that $|\phi_n^+\rangle$ and $|\phi_n^-\rangle$ are orthonormal, the matrix elements of the time evolution operator $\hat{U} = \exp(-i\hat{H}t)$ then read

$$\begin{aligned}
c_n &\equiv \langle 1, n+1 | \hat{U} | 1, n+1 \rangle \\
&= \sin^2 \theta_n e^{-iE_n^+ t} + \cos^2 \theta_n e^{-iE_n^- t}, \\
a_n &\equiv \langle 2, n | \hat{U} | 2, n \rangle \\
&= \cos^2 \theta_n e^{-iE_n^+ t} + \sin^2 \theta_n e^{-iE_n^- t}, \\
b_n &\equiv \langle 2, n | \hat{U} | 1, n+1 \rangle = \langle 1, n+1 | \hat{U} | 2, n \rangle \\
&= \sin \theta_n \cos \theta_n \left(e^{-iE_n^+ t} - e^{-iE_n^- t} \right).
\end{aligned} \tag{3.8}$$

This needs to be supplemented with the matrix elements of \hat{U} in the state $|1, 0\rangle$. From $H|1, 0\rangle = E_1|1, 0\rangle$ we have

$$c_{-1} \equiv \langle 1, 0 | \hat{U} | 1, 0 \rangle = e^{-iE_1 t} = e^{i\Omega t/2}. \tag{3.9}$$

By using $\sin(2\theta_n) = \gamma\sqrt{n+1}/\beta_n$, the transition probability for an atom to emit a photon at time t , when there are n of them in the cavity, can be expressed as

$$|b_n|^2 = \frac{(n+1)\gamma^2}{2\beta_n^2} [1 - \cos(2\beta_n t)], \tag{3.10}$$

which displays the Rabi oscillations [Shore and Knight \(1993\)](#) with the frequency $2\beta_n$ corresponding to the energy gap between the *dressed* atomic states [Haroche and Raimond \(1985\)](#), determined from (3.5).

We focus now on the evolution of the density matrix of the total system from an initial factorized state

$$\hat{\rho}^t = \hat{U} \hat{\rho}^0 \hat{U}^\dagger, \quad \text{with } \hat{\rho}^0 = \hat{\rho} \otimes \hat{\sigma}, \tag{3.11}$$

where $\hat{\varrho} \equiv \hat{\rho}_f^0$ is the initial reduced density matrix of the field and $\hat{\sigma} \equiv \hat{\rho}_a^0$ that for the atoms, and consider the matrix elements of the reduced density matrix of the field at later times

$$\langle n | \hat{\rho}_f^t | n' \rangle = \sum_i \langle i, n | \hat{\rho}^t | i, n' \rangle, \quad (3.12)$$

In terms of the matrix elements of the time evolution operator in (3.8), we have

$$\begin{aligned} \langle n | \hat{\rho}_f^t | n' \rangle &= \sigma_{11} \left[c_{n-1} c_{n'-1}^* \varrho_{n,n'} + b_n b_{n'}^* \varrho_{n+1,n'+1} \right] \\ &+ \sigma_{12} \left[c_{n-1} b_{n'-1}^* \varrho_{n,n'-1} + b_n a_{n'}^* \varrho_{n+1,n'} \right] + \sigma_{21} \left[b_{n-1} c_{n'-1}^* \varrho_{n-1,n'} + a_n b_{n'}^* \varrho_{n,n'+1} \right] \\ &+ \sigma_{22} \left[b_{n-1} b_{n'-1}^* \varrho_{n-1,n'-1} + a_n a_{n'}^* \varrho_{n,n'} \right]. \end{aligned} \quad (3.13)$$

From this result, it is immediately realized that if the initial reduced density matrices of the subsystems are diagonal, i.e.

$$\varrho_{n,n'} = \delta_{nn'} P_n^0, \quad \text{and} \quad \sigma_{ij} = \delta_{ij} \sigma_{ii}, \quad (3.14)$$

then the subsequent reduced density matrices remain diagonal (we show this for the atoms next). In this case, with $|a_n|^2 = |c_n|^2 = 1 - |b_n|^2$, we have for the probability distribution $P_n^t = \langle n | \hat{\rho}_f^t | n \rangle$ of the n -photon states

$$P_n^t = P_n^0 + |b_{n-1}|^2 (\sigma_{22} P_{n-1}^0 - \sigma_{11} P_n^0) - |b_n|^2 (\sigma_{22} P_n^0 - \sigma_{11} P_{n+1}^0). \quad (3.15)$$

For the atoms, we need to trace now over the degrees of freedom of the field. Since we are interested in initial diagonal ensembles for the subsystems, we have

$$\langle i | \hat{\rho}_a^t | j \rangle = \sum_n \langle i, n | \hat{\rho}^t | j, n \rangle = K_{11}^{ij} \sigma_{11} + K_{22}^{ij} \sigma_{22}, \quad (3.16)$$

where we have defined

$$K_{i'i'}^{ij} = \sum_{nn'} \langle i, n | \hat{U} | i', n' \rangle \langle i', n' | \hat{U}^\dagger | j, n \rangle P_{n'}^0. \quad (3.17)$$

In terms of the matrix elements in (3.8), it is easily seen that $K_{i'i'}^{ij} = 0$ for $i \neq j$, which implies that the reduced density matrix of the atom also remains diagonal and then, denoting with $p_i^t = \langle i | \hat{\rho}_a^t | i \rangle$ the occupation probabilities of the atomic states, we have

$$\begin{aligned} p_1^t &= \sigma_{11} + \sum_n |b_n|^2 (\sigma_{22} P_n^0 - \sigma_{11} P_{n+1}^0), \\ p_2^t &= \sigma_{22} - \sum_n |b_n|^2 (\sigma_{22} P_n^0 - \sigma_{11} P_{n+1}^0). \end{aligned} \quad (3.18)$$

With this brief exposition of the Jaynes-Cummings model in mind, we are ready to introduce the puzzle that came with the original introduction of this model.

3.3 Introduction

The Jaynes-Cummings model is a paradigmatic model in quantum optics [Jaynes and Cummings \(1963\)](#); [Shore and Knight \(1993\)](#); [Greentree et al. \(2013\)](#), describing the electric dipole interaction of a two-level atom with a single mode of a quantized electromagnetic field in a cavity. In cavity QED experiments [Haroche and Kleppner \(1989\)](#); [Walther et al. \(2006\)](#), where a beam of Rydberg atoms prepared in a well-defined initial state are sent to a high- Q superconducting cavity—which can be tuned to the resonance frequency of two selected neighboring levels of the atoms—the model has served to understand purely quantum phenomena such as the Rabi oscillations of the level populations, as well as the collapse-and-revival of these oscillations when the field in the cavity is a thermal field [Rempe et al. \(1987\)](#) or a coherent field [Brune et al.](#)

(1996). It also helps elucidating the manifestation of quantum correlations (entanglement) Shore and Knight (1993) with possible applications in quantum information processing Ellinas and Smyrnakis (2005).

Despite its great success, there is still a conceptual puzzle which needs to be understood: if two-level atoms with energy splitting Ω and initial thermal distribution of their states at temperature T_a are sent to a single-mode cavity with frequency ω , with such a flux that the N th atom enters the cavity as the $(N - 1)$ th one leaves it, the steady state of the field is thermal at temperature

$$T_f = (\omega/\Omega) T_a. \quad (3.19)$$

Originally discovered by Jaynes and Cummings (1963) and realized, in principle, in a one-atom maser Meschede et al. (1985); Nogues et al. (1999); Rauschenbeutel et al. (2000), the result (3.19) implies that except at resonance, when $\omega = \Omega$, the two subsystems do not equilibrate their temperatures.

This apparent violation of energy conservation, as first understood Jaynes and Cummings (1963), was attributed to the neglect of the translational degrees of freedom of the atoms, which was argued to make the assumption of “thermal” atoms unjustified. The neglect of losses in the cavity was also considered as a possible source for the lack of temperature equilibration.

The arguments above are, however, not entirely satisfactory, for Cummings himself in an earlier paper Cummings (1962) showed that a two-level atom weakly interacting with an intense black-body radiation field for a very long time, approaches a Boltzmann distribution of the two levels, irrespective of the translational motion. Also, cavities with extremely high- Q values are now possible to build using superconducting materials Walther et al. (2006), rendering the assumption of a lossless cavity a very good approximation.

In this work we show that the lack of temperature equilibration between the two

subsystems can be understood by applying the theory of quantum entropy production that we have recently developed [Solano-Carrillo and Millis \(2016\)](#). We show that when the steady state is approached out of resonance, the field and atoms subsystems become *adiabatically insulated* from each other, with the steady state being an equilibrium state with zero total entropy production. Under this circumstance, the difference of temperatures is not puzzling since an adiabatic “wall” is built up, in the long run, between the subsystems. At resonance, this insulation is not present and equilibration of the temperatures automatically takes place.

3.4 The one-atom maser

In section [3.2](#) we discussed the statistical dynamics of an atom coupled to a single mode of radiation in a cavity. We are interested here in the configuration in which the $(N - 1)$ th atom leaves the cavity when the N th one enters it, which is a possible running mode of a one-atom maser, provided the atomic flux through the cavity is adjusted such that each atom is made to spend a time τ within the cavity.

The so-obtained Markov chain has an irreversible statistical dynamics since we are transferring atoms from one particle reservoir to a different one by passage through the cavity. The way this adds irreversibility to the problem of the closed-system dynamics inside the cavity is similar in nature to Pauli’s repeated random-phase assumption (at each end of a succession of time intervals) of a wavefunction evolved with Schrödinger equation [Pauli \(1928\)](#). As we will see, the probability distribution of the atoms in the present case is initialized to the same value every time a new atom enters the cavity so the time propagation does not satisfy Huygens’ principle. This leads to a loss of unitary evolution and an eventual equilibration of the system.

In [Fig. 3.1](#) we show a set up of the Jaynes-Cumming thought experiment that we have designed for the present discussion. The first cavity on the left is used to

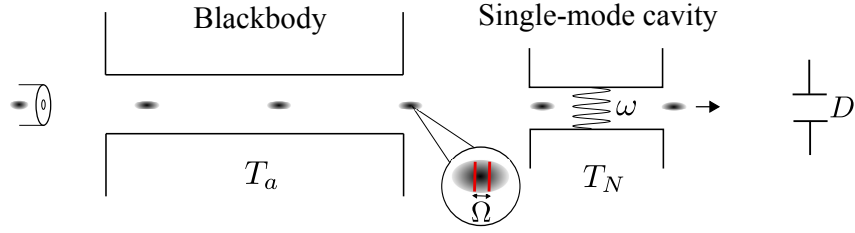


Figure 3.1: Sketch of a set up for the Jaynes-Cummings thought experiment. After two-level atoms are prepared in arbitrary initial states and made to interact *weakly* with a very large number of photons comprising the stochastic electromagnetic field of a blackbody at temperature T_a , the atoms attain, at sufficiently long times, a Boltzmann distribution at temperature T_a Cummings (1962). This is taken as the initial statistical state for the evolution in the presence of a monochromatic field of frequency ω in the second cavity, which can be assigned an effective temperature T_N at the moment when the N th atom enters. The state of the atoms (and hence of the field) after leaving the cavity is probed with a detector D .

prepare two-level atoms with a Boltzmann distribution of their states at temperature T_a after which they are sent to a second cavity to *weakly* interact with a single mode of radiation with frequency ω .

Since the reduced density matrix of the field remains diagonal for all times, we assume that an effective temperature T_N can be defined as that which makes the probability distribution of the field in the second cavity when the N th atom is just entering, a Gibbs distribution at temperature T_N . The validity of this depends on the weak coupling condition (3.2), as fully discussed in the next section.

In Fig. 3.1 each atom then sees a different initial state for the field in the second cavity, which is the final state left by the previous atom so that, denoting

$F_n^t(N)$: probability that the second cavity has n
 photons at time t when the N th atom is
 traversing it,

where $t \in [0, \tau]$, we can rewrite (3.15) as

$$P_n^t(N) = P_n^0(N) + |b_{n-1}|^2 [\sigma_{22}P_{n-1}^0(N) - \sigma_{11}P_n^0(N)] - |b_n|^2 [\sigma_{22}P_n^0(N) - \sigma_{11}P_{n+1}^0(N)], \quad (3.20)$$

where $P_n^0(N) = P_n^\tau(N-1)$ is, by assumption, a thermal distribution at temperature T_N . Likewise (3.18) is rewritten as

$$p_i^t(N) = \sigma_{ii} + (-1)^{i+1} \sum_n |b_n|^2 [\sigma_{22}P_n^0(N) - \sigma_{11}P_{n+1}^0(N)], \quad (3.21)$$

which is *initialized* to σ_{ii} every time a new atom enters. Due to its importance for the subsequent discussion, we prove next that a thermal distribution at temperature T_N when the atoms are just entering the cavity is actually the case for very weak coupling between the atoms and the field.

3.4.1 Thermal Quasi-Equilibrium Distribution of the Photons

The condition of weak coupling in (3.2) is fundamental for the present discussion since only in this case a truly thermodynamic behavior corresponds to the quantum statistics. This is actually realized in practice in cavity QED experiments in which $\gamma/\Omega \sim 10^{-7}$ is easily obtained [Brune et al. \(1994\)](#), with very long decay times for the cavity $\tau_{\text{cav}}/\tau \sim 10^4$ and the atomic states $\tau_{\text{atom}}/\tau \sim 10^3$ [Walther et al. \(2006\)](#).

We assume that it is impossible to have an infinite number of photons in the cavity at any time (e.g. that costs a lot if the photons have nonzero chemical potential) or, equivalently, that an integer M should exist such that, if there are n photons in the cavity, $n \leq M$. The very-weak coupling condition can then be expressed as

$$0 < \gamma\tau \ll M^{-1}. \quad (3.22)$$

By expanding the transition probability $|b_n|$ ² evaluated at time τ in a power series in $\gamma\tau$ we then find, up to the leading order,

$$|b_n^\tau|^2 = (n+1)(\gamma\tau)^2. \quad (3.23)$$

If the probability distribution when the N th atom is entering the cavity is assumed to be thermal at temperature T_N we should have

$$P_n^0(N) = a_N K_N^n, \quad K_N = e^{-\omega/T_N}, \quad (3.24)$$

where $a_N = 1 - K_N$ is the normalization constant. Note that the factor coming from the chemical potential μ is absorbed in the definition of a_N , i.e. $a_N \propto e^{\mu/T_N}$.

When (3.24) is substituted in (3.20) at time τ we have

$$P_n^\tau(N) = a_N K_N^n \left[1 + K_N^{-1}(\sigma_{22} - K_N \sigma_{11})(|b_{n-1}^\tau|^2 - K_N |b_n^\tau|^2) \right]. \quad (3.25)$$

The condition $P_n^\tau(N) = P_n^0(N+1)$ together with (3.24) imply that we must have

$$a_{N+1} K_{N+1}^n = a_N K_N^n \left[1 + K_N^{-1}(\sigma_{22} - K_N \sigma_{11})(|b_{n-1}^\tau|^2 - K_N |b_n^\tau|^2) \right]. \quad (3.26)$$

In order to satisfy this equation it is required that

$$e^{\frac{n\omega(\Delta T_N/T_N)}{T_N + \Delta T_N}} (1 + X_N) = 1 + K_N^{-1}(\sigma_{22} - K_N \sigma_{11})(|b_{n-1}^\tau|^2 - K_N |b_n^\tau|^2). \quad (3.27)$$

Replacing this in (3.26) give the recursive equations

$$a_{N+1} = (1 + X_N) a_N, \quad (3.28)$$

$$T_{N+1} = T_N + \Delta T_N. \quad (3.29)$$

The possibility of having a thermal distribution for the field every time a new atom enters the cavity then relies on the self-consistency of the equations (3.28) and (3.29).

Note that this description is symmetric with respect to making γ very small or instead making τ very small. In the latter case, it is not expected that the effective temperature of the field changes considerably after the passage of an atom and then $\Delta T_N/T_N \ll 1$.

Assuming $X_N \ll 1$ as well, we can then expand the left-hand side of (3.27) and substitute (3.23) in the right-hand side to obtain

$$(\omega/T_N)(\Delta T_N/T_N) = K_N^{-1}(\sigma_{22} - K_N\sigma_{11})(1 - K_N)(\gamma\tau)^2, \quad (3.30)$$

which determines the temperature changes at each step of the discrete dynamics, and

$$X_N = -(\sigma_{22} - K_N\sigma_{11})(\gamma\tau)^2, \quad (3.31)$$

which keeps the probability distribution of the photons normalized.

Using (3.24) we have, in terms of the steady state temperature of the photon field $T_f = (\omega/\Omega) T_a$ (to be derived in the next section)

$$\Delta T_N/T_N = -\operatorname{sech}\left(\frac{\omega}{2T_f}\right) \sinh\left[\frac{\omega}{2}\left(\frac{1}{T_f} - \frac{1}{T_N}\right)\right] \operatorname{sinhc}\left(\frac{\omega}{2T_N}\right) (\gamma\tau)^2. \quad (3.32)$$

This proves the consistency of (3.29) since, beginning with a temperature $T_i = T_{N=1}$ for the field, if $T_i > T_f$, (3.32) says that the field will start cooling as atoms cross the cavity until the temperature of the steady state T_f is reached after which no more temperature changes occur. Heating of the field will happen instead if $T_i < T_f$.

It should be mentioned, as seen from (3.32), that if $\omega/T_f < 1$ the cooling process can take place from *any* initial temperature $T_i > T_f$. However, the heating process can not start from arbitrarily low temperatures since the prefactor of $(\gamma\tau)^2$ in (3.32)

can grow arbitrarily, with the possibility of making $\Delta T_N/T_N \ll 1$ inconsistent. The same reasoning applied to the case $\omega/T_f > 1$ shows that cooling consistently takes place only for sufficiently large initial temperatures.

These observations are in line with the third law of thermodynamics which, in one of its forms, states that the specific heat of materials tend to zero as the temperature goes to zero or, in other words, it is very hard to change the temperature when the system is close to the absolute zero.

We now turn our attention to the consistency of (3.28). This is proven by rewriting that equation, on one hand, in terms of $a_N = 1 - K_N$ and using (3.31)

$$K_{N+1} = K_N + (\sigma_{22} - K_N \sigma_{11})(1 - K_N)(\gamma\tau)^2. \quad (3.33)$$

On the other hand, by expanding K_{N+1} in a Taylor series about $\Delta T_N/T_N = 0$ we easily get, up to leading order,

$$K_{N+1} = K_N + K_N(\omega/T_N)(\Delta T_N/T_N), \quad (3.34)$$

which, after using (3.30), is equivalent to (3.33).

We have therefore proven the consistency of both (3.28) and (3.29) and then the probability distribution of the field every time a new atom enters the cavity is really thermal in the weak coupling limit.

3.4.2 Master equations for the field and the atoms

We now prove the conditions for the steady state in the Jaynes-Cummings thought experiment and prepare the road for the entropy-production calculations in the next section. Introducing the notation for the conditional transition probability rates of

the n -photon states

$$\frac{d}{dt}|b_n|^2 = r_{n,n+1} \stackrel{(3.8)}{=} r_{n+1,n}, \quad (3.35)$$

we have for the transition probability rates of losing or gaining a photon in the second cavity, respectively, from the time a new atom enters up to the time t

$$\begin{aligned} w_{n+1,n} &= \sigma_{11} r_{n+1,n}, \\ w_{n,n+1} &= \sigma_{22} r_{n,n+1}, \end{aligned} \quad (3.36)$$

with $w_{n,n'} = 0$ for $|n - n'| > 1$ and $n = n'$. In this way (3.20) becomes, after differentiation

$$\frac{dP_n^t(N)}{dt} = \sum_{n'} [P_{n'}^0(N) w_{n',n} - P_n^0(N) w_{n,n'}]. \quad (3.37)$$

Similarly, we define the atomic transition probability rates from the time a new atom enters the second cavity up to time t as

$$\begin{aligned} v_{2,1}(N) &= \sum_n P_n^0(N) r_{n,n+1}, \\ v_{1,2}(N) &= \sum_n P_{n+1}^0(N) r_{n+1,n}, \end{aligned} \quad (3.38)$$

with $v_{i,i} = 0$. In terms of these, (3.21) becomes after differentiation

$$\frac{dp_i^t(N)}{dt} = \sum_j [\sigma_{jj} v_{j,i}(N) - \sigma_{ii} v_{i,j}(N)]. \quad (3.39)$$

Equations (3.37) and (3.39), together with the conditions $P_n^0(N) = P_n^\tau(N - 1)$ and $p_i^0(N) = \sigma_{ii}$, are recognized as rate equations for a Markov process. A necessary and sufficient condition for the steady state of the field in the second cavity, for which

$$P_n^t(N) = P_n^0(N) \equiv \mathcal{P}_n, \quad (3.40)$$

when many atoms are sent to it ($N \rightarrow \infty$) is that *detailed balance* is satisfied, that is, from (3.37)

$$\mathcal{P}_{n'} w_{n',n} - \mathcal{P}_n w_{n,n'} = 0, \quad \forall n, n'. \quad (3.41)$$

This is also seen directly from (3.20)—the way Jaynes and Cummings originally did it [Jaynes and Cummings \(1963\)](#)—by demanding that the quantity

$$|b_n|^2 (\sigma_{22} \mathcal{P}_n - \sigma_{11} \mathcal{P}_{n+1}) \quad (3.42)$$

be independent of n , so that the second and third terms in (3.20) cancel each other out. For this quantity to be independent of n , it is necessary that

$$|b_n|^2 (\sigma_{22} \mathcal{P}_n - \sigma_{11} \mathcal{P}_{n+1}) = |b_\infty|^2 (\sigma_{22} \mathcal{P}_\infty - \sigma_{11} \mathcal{P}_{\infty+1}), \quad (3.43)$$

however, since $\sum_n^\infty \mathcal{P}_n = 1$, we must have $\mathcal{P}_\infty = 0$, and then the only way (3.42) is independent of n is by vanishing, giving the condition ($|b_n|^2 \leq 1$ and only vanishes for isolated values of n)

$$\frac{\mathcal{P}_n}{\mathcal{P}_{n+1}} = \frac{\sigma_{11}}{\sigma_{22}}, \quad (3.44)$$

which is just (3.41) after using (3.35) and (3.36). It is clearly seen from (3.21) that when the field in the second cavity reaches a steady state, the probability distribution of the subsequent atoms is unaltered by crossing the second cavity, since each term in the sum in (3.21) is of the form (3.42), which was shown to vanish for all n .

Since the atoms leave the first cavity with a Boltzmann distribution of their states at temperature T_a , we have $\sigma_{22}/\sigma_{11} = e^{-\Omega/T_a}$ and then, if an effective temperature T_f is to be assigned to the steady state of the field, so that $\mathcal{P}_{n+1}/\mathcal{P}_n = e^{-\omega/T_f}$, Eq. (3.44) implies that

$$\frac{\omega}{T_f} = \frac{\Omega}{T_a}, \quad (3.45)$$

which is the same as (3.19), that is, only at resonance the two subsystems equilibrate

their temperatures.

3.5 Entropy production

We summarize in this section the general considerations of the theory developed in the previous chapter, followed by how this is applied in the present problem.

3.5.1 General considerations

We have discussed in [Solano-Carrillo and Millis \(2016\)](#) that, just as a hermitian operator \hat{A} is assigned to every observable in quantum mechanics, thermodynamic observables are also represented by operators which vary sufficiently slow. These are obtained by the projection $\hat{\mathcal{A}} = \mathcal{D}\hat{A}$ of the quantum observable \hat{A} to the Hilbert space spanned by the stationary states $\{|\alpha\rangle\}$ of the Hamiltonian $\hat{\mathcal{H}}$ representing the energy of *independent* degrees of freedom (uncoupled subsystems), with \mathcal{D} being the corresponding projection operator.

For every isolated system, the Hamiltonian can be written as $\hat{H} = \hat{\mathcal{H}} + \hat{V}$, with \hat{V} being the potential mixing all (or a set of) the degrees of freedom left uncoupled by $\hat{\mathcal{H}}$. The evolution of the state, represented by the density matrix $\hat{\rho}_t$, is unitarily generated by \hat{H} and the quantum observable corresponding to entropy is $\hat{S}_t = -\ln \hat{\rho}_t$.

According to our definition, the part which is observed in thermodynamic phenomena is $\hat{\mathcal{S}}_t = \mathcal{D}\hat{S}_t$, i.e.

$$\hat{\mathcal{S}}_t = -\mathcal{D} \ln \hat{\rho}_t, \quad (3.46)$$

as can be shown in general by taking its expectation value, which we call the thermodynamic entropy, and noting that it rigorously satisfies the three laws of thermodynamics.

The rate of change of the thermodynamic entropy operator satisfies the equation

$$i\partial_t \hat{\mathcal{S}}_t = \mathcal{D}L\hat{\mathcal{S}}_t + \mathcal{D}Le^{-itNL}\mathcal{N}\hat{\mathcal{S}}_0 - i \int_0^t d\tau K_\tau \hat{\mathcal{S}}_{t-\tau}, \quad (3.47)$$

where $\mathcal{N} = 1 - \mathcal{D}$ projects operators to their nondiagonal parts, $L = [\hat{H}, \cdot]$ is the Liouville superoperator corresponding to \hat{H} and $K_\tau = \mathcal{D}e^{-itNL}L\mathcal{N}L$ is known as the memory kernel. We use ∂_t in this section as a short-hand notation for $\partial/\partial t$.

For initial states of the local equilibrium form (which are diagonal) and for very weak coupling of the subsystems, the long-time evolution is Markovian, i.e. (3.47) becomes memoryless

$$i\partial_t \hat{\mathcal{S}}_t = - \lim_{s \rightarrow 0^+} K_s \hat{\mathcal{S}}_t,$$

with K_s being the Laplace transform of K_τ . The expectation value of this equation leads to

$$\langle \partial_t \hat{\mathcal{S}}_t \rangle = \sum_{\alpha\alpha'} P_\alpha W_{\alpha\alpha'} \ln \frac{P_\alpha}{P_{\alpha'}}, \quad (3.48)$$

with the transition rates $W_{\alpha\alpha'} = 2\pi\delta(\varepsilon_\alpha - \varepsilon_{\alpha'})|V_{\alpha\alpha'}|^2$, calculated in the lowest order in the coupling potential and $P_\alpha = \langle \alpha | \hat{\rho}_t | \alpha \rangle$ being the occupation probability of the state $|\alpha\rangle$ in its lowest-order approximation, satisfying the transport or Pauli master equation

$$\partial_t P_\alpha = \sum_{\alpha'} (P_{\alpha'} W_{\alpha'\alpha} - P_\alpha W_{\alpha\alpha'}). \quad (3.49)$$

Eq. (3.48), which can alternatively be derived by writing the thermodynamic entropy in this approximation as

$$\langle \hat{\mathcal{S}}_t \rangle = - \sum_{\alpha} P_\alpha \ln P_\alpha, \quad (3.50)$$

differentiating and using (3.49), has the same form as the entropy production of an aged *classical* Markovian system with gaussian fluctuations, where the α is in this

case interpreted as a realization of the deviation of the thermodynamic (extensive) variables from their equilibrium values.

A special situation occurs when the coupling between subsystems is so weak that they can be treated as statistically uncorrelated as a first approximation. In this case, the thermodynamic entropy becomes additive and an equation like (3.49) holds for the diagonal entries of the reduced density matrix of each subsystem.

Very weak coupling implies that equilibration within each subsystem takes places much faster than among them and hence, if left alone, the long-time state of the system is one of local equilibrium, described by the factorized density matrix

$$\hat{\varrho}^r = \bigotimes_l \hat{\varrho}_l^r = \bigotimes_l \exp[-(\hat{\mathcal{H}}_l - \mu_l \hat{\mathcal{N}}_l - \Omega_l)/T_l], \quad (3.51)$$

with l labeling the different uncorrelated subsystems, with temperature T_l , chemical potential μ_l and thermodynamic potential $\Omega_l = \Omega_l(T_l, \mu_l, \{x_\lambda^l\})$; the latter defined through the normalization of the density matrix, requiring $\text{Tr} \exp[-(\hat{\mathcal{H}}_l - \mu_l \hat{\mathcal{N}}_l)/T_l] = \exp(-\Omega_l/T_l)$.

The quantities $\{x_\lambda^l\}$ are a set of external parameters for subsystem l upon which its Hamiltonian $\hat{\mathcal{H}}_l$ depends; these parameterize the action of the operator which couples the degrees of freedom of the subsystem l to those of the other subsystems, and $\hat{\mathcal{N}}_l$ is the operator corresponding to the number of particles.

Since (3.51) is expressed in terms of (diagonal) thermodynamic operators, the thermodynamic entropy operator from (3.46) and (3.51) is

$$\hat{\mathcal{S}}^r = -\ln \hat{\varrho}^r = \frac{1}{T_l} \sum_l (\hat{\mathcal{H}}_l - \mu_l \hat{\mathcal{N}}_l - \Omega_l). \quad (3.52)$$

The equation corresponding to (3.48) is easily shown to be the sum over all subsystems

of the contributions $\langle d\hat{\mathcal{S}}_i^r \rangle$ obtained from

$$T_i \langle d\hat{\mathcal{S}}_i^r \rangle = \langle d\hat{\mathcal{H}}_i \rangle - \mu_i \langle d\hat{\mathcal{N}}_i \rangle + \sum_{\lambda} F_{\lambda}^l dx_{\lambda}^l, \quad (3.53)$$

where $F_{\lambda}^l = -\langle \partial \hat{\mathcal{H}}_i / \partial x_{\lambda}^l \rangle$. This may be written as the well-known form of the first law of thermodynamics

$$T_i \partial_t \langle \hat{\mathcal{S}}_i^r \rangle = \partial_t \langle \hat{\mathcal{H}}_i \rangle - \mu_i \partial_t \langle \hat{\mathcal{N}}_i \rangle + \sum_{\lambda} F_{\lambda}^l \partial_t x_{\lambda}^l, \quad (3.54)$$

provided the process takes place slowly enough, a condition which can be stated as $\|\partial_t \hat{\rho}^f\|$ being very small, in a norm defined in [Solano-Carrillo and Millis \(2016\)](#).

When the continuity equations for the local average energy and number of particles is used in (3.54), an expression for the total entropy production $\Pi = \partial_t \langle \hat{\mathcal{S}}^r \rangle$ in the system can then be obtained. This will be done for the particular case of two subsystems in contact in the following section.

3.5.2 Application to the one-atom maser

The dynamics of the Jaynes-Cummings model is special because, in the basis $\{|\alpha\rangle\} = \{|1, n+1\rangle, |2, n\rangle\}$, the diagonal entries of the reduced density matrices of each subsystem undergoes Markovian evolution (as in (2.53)) independent of the strength of the coupling γ , as expressed by equations (3.37) and (3.39).

The very weak coupling condition enters the calculation of the thermodynamic entropy when correlations between the field and atoms are considered negligible to a first approximation so that (3.50) is additive among subsystems

$$\mathcal{S}_N^t = - \sum_i p_i^t(N) \ln p_i^t(N) - \sum_n P_n^t(N) \ln P_n^t(N).$$

After using the conservation of probabilities, we then have for the entropy production

$$\Pi_N^t = d\mathcal{S}_N^t/dt$$

$$\Pi_N^t = - \sum_i \frac{dp_i^t(N)}{dt} \ln p_i^t(N) - \sum_n \frac{dP_n^t(N)}{dt} \ln P_n^t(N). \quad (3.55)$$

Since the state of the field is monitored through the atoms when these just leave the second cavity, we calculate (3.55) at time $t = \tau$ by using (3.37) and (3.39)

$$\Pi_N^\tau = \left(\frac{\Omega}{T_a} - \frac{\omega}{T_{N+1}} \right) J_N^P, \quad (3.56)$$

where J_N^P is the photon current from the field to the N th atom when this is just leaving the second cavity

$$J_N^P = \sum_n [P_{n+1}^0(N) w_{n+1,n} - P_n^0(N) w_{n,n+1}], \quad (3.57)$$

with the w 's evaluated at time $t = \tau$. In arriving at this result, we have used the fact that p_i^τ is initialized to $p_i^0 = \sigma_{ii}$, by construction, and that the state of the field each time a new atom enters the cavity can be assigned an effective temperature T_N , i.e.

$$P_{n+1}^0(N)/P_n^0(N) = e^{-\omega/T_N}.$$

This corresponds to the local equilibrium state discussed in (3.51) here evolving under a discrete dynamics: every time a new atom enters the cavity, both the atom and the photon field are thermal.

The discussion in the previous section then suggests that the entropy production calculated in (3.56) should be directly connected to that obtained using the arguments after (3.54). To this end, consider two classical subsystems which are in contact at temperatures T_1 and T_2 and respective chemical potentials μ_1 and μ_2 . The total

entropy production Π for this system is

$$\Pi = \frac{1}{T_1} \frac{\delta Q_1}{dt} + \frac{1}{T_2} \frac{\delta Q_2}{dt}, \quad (3.58)$$

where δQ_i is the quantity of heat exchanged by the subsystem i with the other subsystem during a time interval dt , which is expressed at constant volume (constraints specified by the x_λ^i in (3.54) kept *fixed*) by

$$\delta Q_i = dE_i - \mu_i dN_i, \quad (3.59)$$

where E_i and N_i are, respectively, the average internal energy and number of particles of subsystem i . Using the conservation of energy and particles we have, in terms of the energy current J^E and a particle current J^P

$$J^E = \frac{dE_1}{dt} = -\frac{dE_2}{dt}, \quad J^P = \frac{dN_1}{dt} = -\frac{dN_2}{dt}. \quad (3.60)$$

Substituting (3.59) and (3.60) in (3.58), we can write the total entropy production as the sum $\Pi = \Pi^E + \Pi^P$ of the contributions from the two irreversible processes taking place: energy transport and particle diffusion, with the respective terms given by

$$\Pi = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) J^E + \left(\frac{\mu_2}{T_2} - \frac{\mu_1}{T_1} \right) J^P. \quad (3.61)$$

Thermodynamic equilibrium between the subsystems is characterized by the vanishing of the thermodynamic forces (quantities in parentheses in (3.61)) and the respective induced currents, and therefore of the total entropy production. This leads to the well-known conditions for equilibrium $T_1 = T_2$ and $\mu_1 = \mu_2$.

Having in mind these considerations, we observe that when the steady state of

the field in the second cavity is approached,

$$P_n^0(N) \rightarrow \mathcal{P}_n \quad \therefore \quad T_N \rightarrow T_f.$$

By using (3.45) and the detailed balance condition (3.41) in (3.56) and (3.57) we then see that both the thermodynamic force (quantity in parentheses in (3.56)) and the induced current vanish in the steady state and hence the total entropy production. This shows that the steady state is a state of thermodynamic equilibrium.

An even more interesting insight is obtained when the nature of the transport processes with which equilibrium is approached in the second cavity is inquired. Since the particles being transported between the atoms and the field are photons, at resonance when $\omega = \Omega$ the energy current is $J^E = \omega J^P = \Omega J^P$ and then in (3.56) we have $\Pi_N^\tau \rightarrow (1/T_a - 1/T_f)J^E$, which is of the form Π^E in (3.61). Out of resonance, when $\omega \neq \Omega$, we see instead that $\Pi_N^\tau \rightarrow (\Omega/T_a - \omega/T_f)J^P$, which is of the form Π^P in (3.61), with $-\omega$ and $-\Omega$ playing the role of chemical potentials for the field and atoms, respectively.

We note that in obtaining the above description of the problem, we have pictured the dressed photons as having a chemical potential which is different (when $\omega \neq \Omega$) depending on whether these belong to the cavity field or to the atoms. A photon “belonging” to an atom is thought as absorbed by the atom, with the potential of giving it back to the field.

This identification of the chemical potential of the photons in the cavity, interacting with the atoms, requires abandoning the common belief that a vanishing chemical potential is a property of all photons (as in a black-body field), which is not generally so [Würfel \(1982\)](#). The chemical potential of radiation depends on the emitter and can even be positive if the latter has an energy gap through which the radiative transitions occur.

The remarks above therefore provide us with an interpretation of the results of

the Jaynes-Cummings thought experiment. At resonance, energy transport is active when approaching the steady state and particle diffusion is absent (impermeable wall building up between the subsystems), a reason why the temperatures of the atoms and field equilibrate. Out of resonance only particle diffusion is active and energy transport is absent (adiabatic wall building up between the subsystems) and then the temperatures do not equilibrate.

The interference of different irreversible processes taking place in a thermodynamic system is basically a classical phenomenon formalized long ago by [Onsager \(1931\)](#). The fact that in the present situation, and under our interpretation, the processes become mutually exclusive depending on the detuning conditions of the cavity is a fully quantum-mechanical phenomenon: we are dealing with single atoms and photons.

3.6 Summary

By calculating the quantum entropy production in a system of atoms weakly interacting with a cavity field and comparing it to the classical results expected for a Markovian evolution, we have been able to infer the nature of the processes with which the steady state in a one-atom maser is approached both at resonance and out of resonance. In particular, we have shown that the lack of equilibration of temperatures of the subsystems in the off-resonant situation is consistent with the equilibrium state attained by two subsystems in contact but adiabatically insulated from each other. At resonance, this insulation is not present and therefore the temperatures do equilibrate. The results presented here are representative of the new kind of information which can be gained by applying quantum-thermodynamic methods.

PHYSICAL REVIEW E **94**, 062116 (2016)**Entropy production and thermalization in the one-atom maser**

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(Received 7 September 2016; revised manuscript received 11 November 2016; published 12 December 2016)

In the configuration in which two-level atoms with an initial thermal distribution of their states are sent in succession to a cavity sustaining a single mode of electromagnetic radiation, one atom leaving the cavity as the next one enters it (as in the one-atom maser), Jaynes and Cummings showed that the steady state of the field, when many atoms have traversed the cavity, is thermal with a temperature different than that of the atoms in the off-resonant situation. Having an interaction between two subsystems which maintains them at different temperatures was then understood as leading to an apparent violation of energy conservation. Here we show, by calculating the quantum entropy production in the system, that this difference of temperatures is consistent with having the subsystems adiabatically insulated from each other as the steady state is approached. At resonance the insulation is removed and equilibration of the temperatures is achieved.

DOI: 10.1103/PhysRevE.94.062116

I. INTRODUCTION

The Jaynes-Cummings model is a paradigmatic model in quantum optics [1–3]. It describes the electric dipole interaction of a two-level atom with a single mode of a quantized electromagnetic field in a cavity. In cavity QED experiments [4,5], where a beam of Rydberg atoms prepared in a well-defined initial state are sent to a high- Q superconducting cavity (which can be tuned to the resonance frequency of two selected neighboring levels of the atoms), the model has served to understand purely quantum phenomena such as the Rabi oscillations of the level populations, as well as the collapse-and-revival of these oscillations when the field in the cavity is a thermal field [6] or a coherent field [7]. It also helps elucidating the manifestation of quantum correlations (entanglement) [2] with possible applications in quantum information processing [8].

Despite its great success, there is still a conceptual puzzle which needs to be understood: if two-level atoms with energy splitting Ω and initial thermal distribution of their states at temperature T_a are sent to a single-mode cavity with frequency ω , with such a flux that the N th atom enters the cavity as the $(N - 1)$ th one leaves it, the steady state of the field is thermal at temperature

$$T_f = (\omega/\Omega) T_a. \quad (1)$$

Originally discovered by Jaynes and Cummings [1] and realized, in principle, in a one-atom maser [9–11], the result (1) implies that except at resonance, when $\omega = \Omega$, the two subsystems do not equilibrate their temperatures.

This apparent violation of energy conservation, as first understood [1], was attributed to the neglect of the translational degrees of freedom of the atoms, which was argued to make the assumption of “thermal” atoms unjustified. The neglect of losses in the cavity was also considered as a possible source for the lack of temperature equilibration.

The arguments above are, however, not entirely satisfactory, for Cummings himself in an earlier paper [12] showed that a two-level atom weakly interacting with an intense black-body radiation field for a very long time, approaches a Boltzmann distribution of the two levels, irrespective of the translational motion. Also, cavities with extremely high- Q values are

now possible to build using superconducting materials [5], rendering the assumption of a lossless cavity a very good approximation.

In this paper we show that the lack of temperature equilibration between the two subsystems can be understood by applying the theory of quantum entropy production that we have recently developed [13]. We show that when the steady state is approached out of resonance, the field and atoms subsystems become *adiabatically insulated* from each other, with the steady state being an equilibrium state with zero total entropy production. Under this circumstance, the difference of temperatures is not puzzling since an adiabatic “wall” is built up, in the long run, between the subsystems. At resonance, this insulation is not present and equilibration of the temperatures automatically takes place.

In order to make the exposition as complete as possible we organize the paper as follows: in Sec. II we briefly review the important features of the Jaynes-Cummings physics which are relevant for our discussion. In Sec. III we discuss the aforementioned configuration of the one-atom maser including the derivation of (1). In Sec. IV we calculate the entropy production in the Jaynes-Cummings thought experiment, show how it tends to its steady state value, and compare it with expectations from classical nonequilibrium thermodynamics. We conclude with Sec. V.

II. JAYNES-CUMMINGS MODEL

The Jaynes-Cummings model describes the electric dipole coupling of a quantized single mode (energy ω) of electromagnetic radiation in a cavity, with a two-level atom with energy splitting $\Omega = E_2 - E_1$. The Hamiltonian describing the cavity field + atom system is, in the rotating wave approximation,

$$\hat{H} = E_1 \hat{\pi} \hat{\pi}^\dagger + E_2 \hat{\pi}^\dagger \hat{\pi} + \omega \hat{a}^\dagger \hat{a} + \gamma (\hat{\pi}^\dagger \hat{a} + \hat{\pi} \hat{a}^\dagger), \quad (2)$$

where \hat{a}^\dagger (\hat{a}) is the creation (annihilation) operator of a photon in the cavity, $\hat{\pi}^\dagger$ and $\hat{\pi}$ are the ladder operators for the atomic states, and γ is the strength of the dipole coupling, assumed small (see the Appendix):

$$\gamma \ll \Omega. \quad (3)$$

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We work in the natural basis $\{|\alpha\rangle\} = \{|1, n+1\rangle, |2, n\rangle\}$ which diagonalizes the Hamiltonian of *uncoupled* subsystems $\hat{\mathcal{H}} = E_1 \hat{\pi} \hat{\pi}^\dagger + E_2 \hat{\pi}^\dagger \hat{\pi} + \omega \hat{a}^\dagger \hat{a}$, where $\{|1\rangle, |2\rangle\}$ are the two states of the atom (ground and excited), with

$$\hat{\pi}^\dagger |1\rangle = |2\rangle, \quad \hat{\pi}^\dagger |2\rangle = 0, \quad \hat{\pi} |2\rangle = |1\rangle, \quad \hat{\pi} |1\rangle = 0, \quad (4)$$

and n is the number of photons in the cavity. In the sector with n photons, the matrix representation H_n of the total Hamiltonian then reads

$$H_n = \begin{pmatrix} E_1 + (n+1)\omega & \gamma\sqrt{n+1} \\ \gamma\sqrt{n+1} & E_2 + n\omega \end{pmatrix}, \quad (5)$$

with $H = \bigoplus_n H_n$. Defining the atomic zero of energy so that $E_1 + E_2 = 0$, we get for the eigenvalues of H_n

$$E_n^\pm = (n+1/2)\omega \pm \beta_n, \quad (6)$$

with $2\beta_n = \sqrt{(\Omega - \omega)^2 + 4(n+1)\gamma^2}$ and the corresponding eigenvectors

$$\begin{aligned} |\phi_n^+\rangle &= \cos\theta_n |2, n\rangle + \sin\theta_n |1, n+1\rangle, \\ |\phi_n^-\rangle &= -\sin\theta_n |2, n\rangle + \cos\theta_n |1, n+1\rangle, \end{aligned} \quad (7)$$

with θ_n indicating the angle of rotation of the basis vectors defining the n -photon sector, where

$$\tan(2\theta_n) = \frac{2\gamma\sqrt{n+1}}{\Omega - \omega}. \quad (8)$$

Inverting (7) and noting that $|\phi_n^+\rangle$ and $|\phi_n^-\rangle$ are orthonormal, the matrix elements of the time evolution operator $\hat{U} = \exp(-i\hat{H}t)$ then read

$$\begin{aligned} c_n &\equiv \langle 1, n+1 | \hat{U} | 1, n+1 \rangle \\ &= \sin^2\theta_n e^{-iE_n^+ t} + \cos^2\theta_n e^{-iE_n^- t}, \\ a_n &\equiv \langle 2, n | \hat{U} | 2, n \rangle \\ &= \cos^2\theta_n e^{-iE_n^+ t} + \sin^2\theta_n e^{-iE_n^- t}, \\ b_n &\equiv \langle 2, n | \hat{U} | 1, n+1 \rangle = \langle 1, n+1 | \hat{U} | 2, n \rangle \\ &= \sin\theta_n \cos\theta_n (e^{-iE_n^+ t} - e^{-iE_n^- t}). \end{aligned} \quad (9)$$

This needs to be supplemented with the matrix elements of \hat{U} in the state $|1, 0\rangle$. From $H|1, 0\rangle = E_1|1, 0\rangle$ we have

$$c_{-1} \equiv \langle 1, 0 | \hat{U} | 1, 0 \rangle = e^{-iE_1 t} = e^{i\Omega t/2}. \quad (10)$$

By using $\sin(2\theta_n) = \gamma\sqrt{n+1}/\beta_n$, the transition probability for an atom to emit a photon at time t , when there are n of them in the cavity, can be expressed as

$$|b_n|^2 = \frac{(n+1)\gamma^2}{2\beta_n^2} [1 - \cos(2\beta_n t)], \quad (11)$$

which displays the Rabi oscillations [2] with the frequency $2\beta_n$ corresponding to the energy gap between the *dressed* atomic states [14], determined from (6).

We focus now on the evolution of the density matrix of the total system from an initial factorized state

$$\hat{\rho}^t = \hat{U} \hat{\rho}^0 \hat{U}^\dagger, \quad \text{with } \hat{\rho}^0 = \hat{\rho} \otimes \hat{\sigma}, \quad (12)$$

where $\hat{\rho} \equiv \hat{\rho}_f^0$ is the initial reduced density matrix of the field and $\hat{\sigma} \equiv \hat{\rho}_a^0$ that for the atoms, and consider the matrix

elements of the reduced density matrix of the field at later times

$$\langle n | \hat{\rho}_f^t | n' \rangle = \sum_i \langle i, n | \hat{\rho}^t | i, n' \rangle, \quad (13)$$

In terms of the matrix elements of the time evolution operator in (9), we have

$$\begin{aligned} \langle n | \hat{\rho}_f^t | n' \rangle &= \sigma_{11} [c_{n-1} c_{n'-1}^* \varrho_{n, n'} + b_n b_{n'}^* \varrho_{n+1, n'+1}] \\ &\quad + \sigma_{12} [c_{n-1} b_{n'-1}^* \varrho_{n, n'-1} + b_n a_{n'}^* \varrho_{n+1, n'}] \\ &\quad + \sigma_{21} [b_{n-1} c_{n'-1}^* \varrho_{n-1, n'} + a_n b_{n'}^* \varrho_{n, n'+1}] \\ &\quad + \sigma_{22} [b_{n-1} b_{n'-1}^* \varrho_{n-1, n'-1} + a_n a_{n'}^* \varrho_{n, n'}]. \end{aligned} \quad (14)$$

From this result, it is immediately realized that if the initial reduced density matrices of the subsystems are diagonal,

$$\varrho_{n, n'} = \delta_{nn'} P_n^0, \quad \text{and} \quad \sigma_{ij} = \delta_{ij} \sigma_{ii}, \quad (15)$$

then the subsequent reduced density matrices remain diagonal (we show this for the atoms next). In this case, with $|a_n|^2 = |c_n|^2 = 1 - |b_n|^2$, we have for the probability distribution $P_n^t = \langle n | \hat{\rho}_f^t | n \rangle$ of the n -photon states

$$\begin{aligned} P_n^t &= P_n^0 + |b_{n-1}|^2 (\sigma_{22} P_{n-1}^0 - \sigma_{11} P_n^0) \\ &\quad - |b_n|^2 (\sigma_{22} P_n^0 - \sigma_{11} P_{n+1}^0). \end{aligned} \quad (16)$$

For the atoms, we need to trace now over the degrees of freedom of the field. Since we are interested in initial diagonal ensembles for the subsystems, we have

$$\langle i | \hat{\rho}_a^t | j \rangle = \sum_n \langle i, n | \hat{\rho}^t | j, n \rangle = K_{11}^{ij} \sigma_{11} + K_{22}^{ij} \sigma_{22}, \quad (17)$$

where we have defined

$$K_{ii'}^{ij} = \sum_{nn'} \langle i, n | \hat{U} | i', n' \rangle \langle i', n' | \hat{U}^\dagger | j, n \rangle P_{n'}^0. \quad (18)$$

In terms of the matrix elements in (9), it is easily seen that $K_{ii'}^{ij} = 0$ for $i \neq j$, which implies that the reduced density matrix of the atom also remains diagonal, and then, denoting with $p_i^t = \langle i | \hat{\rho}_a^t | i \rangle$ the occupation probabilities of the atomic states, we have

$$\begin{aligned} p_1^t &= \sigma_{11} + \sum_n |b_n|^2 (\sigma_{22} P_n^0 - \sigma_{11} P_{n+1}^0), \\ p_2^t &= \sigma_{22} - \sum_n |b_n|^2 (\sigma_{22} P_n^0 - \sigma_{11} P_{n+1}^0). \end{aligned} \quad (19)$$

III. THE ONE-ATOM MASER

So far we have discussed the statistical dynamics of an atom coupled to a single mode of radiation in a cavity. We are interested, however, in the configuration in which the $(N-1)$ th atom leaves the cavity when the N th one enters it, which is a possible running mode of a one-atom maser, provided the atomic flux through the cavity is adjusted such that each atom is made to spend a time τ within the cavity.

In Fig. 1 we show a set up of the Jaynes-Cumming thought experiment that we have designed for the present discussion. The first cavity on the left is used to prepare two-level atoms with a Boltzmann distribution of their states at temperature T_a

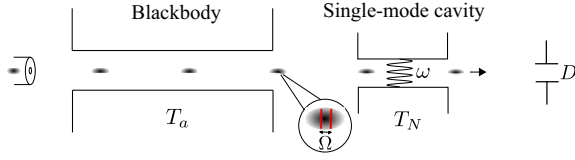


FIG. 1. Sketch of a setup for the Jaynes-Cummings thought experiment. After two-level atoms are prepared in arbitrary initial states and made to interact *weakly* with a very large number of photons comprising the stochastic electromagnetic field of a blackbody at temperature T_a , the atoms attain, at sufficiently long times, a Boltzmann distribution at temperature T_a [12]. This is taken as the initial statistical state for the evolution in the presence of a monochromatic field of frequency ω in the second cavity, which can be assigned an effective temperature T_N at the moment when the N th atom enters. The state of the atoms (and hence of the field) after leaving the cavity is probed with a detector D .

after which they are sent to a second cavity to *weakly* interact with a single mode of radiation with frequency ω .

Since the reduced density matrix of the field remains diagonal for all times, we assume that an effective temperature T_N can be defined as that which makes the probability distribution of the field in the second cavity when the N th atom is just entering, a Gibbs distribution at temperature T_N . The validity of this depends on the weak coupling condition (3), as fully discussed in the Appendix.

The only difference with the discussion in the previous section is that each atom now sees a different initial state for the field in the second cavity, which is the final state left by the previous atom so that, denoting

$P_n^t(N)$: probability that the second cavity has n photons at time t when the N th atom is traversing it,

where $t \in [0, \tau]$, we can rewrite (16) as

$$P_n^t(N) = P_n^0(N) + |b_{n-1}|^2 [\sigma_{22} P_{n-1}^0(N) - \sigma_{11} P_n^0(N)] - |b_n|^2 [\sigma_{22} P_n^0(N) - \sigma_{11} P_{n+1}^0(N)], \quad (20)$$

where $P_n^0(N) = P_n^\tau(N-1)$ is a thermal distribution at temperature T_N . Likewise (19) is rewritten as

$$p_i^t(N) = \sigma_{ii} + (-1)^{i+1} \sum_n |b_n|^2 \times [\sigma_{22} P_n^0(N) - \sigma_{11} P_{n+1}^0(N)], \quad (21)$$

which is *initialized* to σ_{ii} every time a new atom enters.

A more suggestive description is however obtained when these equations are differentiated with respect to time. Introducing the notation for the conditional transition probability rates of the n -photon states

$$\frac{d}{dt} |b_n|^2 = r_{n,n+1} \stackrel{(9)}{=} r_{n+1,n}, \quad (22)$$

we have for the transition probability rates of loosing or gaining a photon in the second cavity, respectively, from the time a new atom enters up to the time t

$$w_{n+1,n} = \sigma_{11} r_{n+1,n}, \quad w_{n,n+1} = \sigma_{22} r_{n,n+1}, \quad (23)$$

with $w_{n,n'} = 0$ for $|n - n'| > 1$ and $n = n'$. In this way (20) becomes, after differentiation

$$\frac{dP_n^t(N)}{dt} = \sum_{n'} [P_{n'}^0(N) w_{n',n} - P_n^0(N) w_{n,n'}]. \quad (24)$$

Similarly, we define the atomic transition probability rates from the time a new atom enters the second cavity up to time t as

$$v_{2,1}(N) = \sum_n P_n^0(N) r_{n,n+1}, \\ v_{1,2}(N) = \sum_n P_{n+1}^0(N) r_{n+1,n}, \quad (25)$$

with $v_{i,i} = 0$. In terms of these, (21) becomes after differentiation

$$\frac{dp_i^t(N)}{dt} = \sum_j [\sigma_{jj} v_{j,i}(N) - \sigma_{ii} v_{i,j}(N)]. \quad (26)$$

Equations (24) and (26), together with the conditions $P_n^0(N) = P_n^\tau(N-1)$ and $p_i^0(N) = \sigma_{ii}$, are recognized as rate equations for a Markov process. A necessary and sufficient condition for the steady state of the field in the second cavity, for which

$$P_n^t(N) = P_n^0(N) \equiv \mathcal{P}_n, \quad (27)$$

when many atoms are sent to it ($N \rightarrow \infty$) is that *detailed balance* is satisfied, that is, from (24)

$$\mathcal{P}_{n'} w_{n',n} - \mathcal{P}_n w_{n,n'} = 0, \quad \forall n, n'. \quad (28)$$

This is also seen directly from (20) by demanding that the quantity

$$|b_n|^2 (\sigma_{22} \mathcal{P}_n - \sigma_{11} \mathcal{P}_{n+1}) \quad (29)$$

be independent of n , so that the second and third terms in (20) cancel each other out. For this quantity to be independent of n , it is necessary that

$$|b_n|^2 (\sigma_{22} \mathcal{P}_n - \sigma_{11} \mathcal{P}_{n+1}) = |b_\infty|^2 (\sigma_{22} \mathcal{P}_\infty - \sigma_{11} \mathcal{P}_{\infty+1}); \quad (30)$$

however, since $\sum_n^\infty \mathcal{P}_n = 1$, we must have $\mathcal{P}_\infty = 0$, and then the only way (29) is independent of n is by vanishing, giving the condition ($|b_n|^2 \leq 1$ and vanishes only for isolated values of n)

$$\frac{\mathcal{P}_n}{\mathcal{P}_{n+1}} = \frac{\sigma_{11}}{\sigma_{22}}, \quad (31)$$

which is just (28) after using (22) and (23). It is clearly seen from (21) that when the field in the second cavity reaches a steady state, the probability distribution of the subsequent atoms is unaltered by crossing the second cavity, since each term in the sum in (21) is of the form (29), which was shown to vanish for all n .

Since the atoms leave the first cavity with a Boltzmann distribution of their states at temperature T_a , we have $\sigma_{22}/\sigma_{11} = e^{-\Omega/T_a}$ and then, if an effective temperature T_f is to be assigned to the steady state of the field, so that $\mathcal{P}_{n+1}/\mathcal{P}_n = e^{-\omega/T_f}$, Eq. (31) implies that

$$\frac{\omega}{T_f} = \frac{\Omega}{T_a}, \quad (32)$$

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which is the same as (1), that is, only at resonance the two subsystems equilibrate their temperatures.

IV. ENTROPY PRODUCTION

A. General considerations

We have discussed in Ref. [13] that, just as a Hermitian operator \hat{A} is assigned to every observable in quantum mechanics, thermodynamic observables are also represented by operators which vary sufficiently slowly. These are obtained by the projection $\hat{\mathcal{A}} = \mathcal{D}\hat{A}$ of the quantum observable \hat{A} to the Hilbert space spanned by the stationary states $\{|\alpha\rangle\}$ of the Hamiltonian $\hat{\mathcal{H}}$ representing the energy of *independent* degrees of freedom (uncoupled subsystems), with \mathcal{D} being the corresponding projection operator.

For every isolated system, the Hamiltonian can be written as $\hat{H} = \hat{\mathcal{H}} + \hat{V}$, with \hat{V} being the potential mixing all (or a set of) the degrees of freedom left uncoupled by $\hat{\mathcal{H}}$. The evolution of the state, represented by the density matrix $\hat{\rho}_t$, is unitarily generated by \hat{H} and the quantum observable corresponding to entropy is $\hat{\mathcal{S}}_t = -\ln \hat{\rho}_t$.

According to our definition, the part which is observed in thermodynamic phenomena is $\hat{\mathcal{S}}_t = \mathcal{D}\hat{\mathcal{S}}_t$, or in terms of the density matrix,

$$\hat{\mathcal{S}}_t = -\mathcal{D} \ln \hat{\rho}_t, \quad (33)$$

as can be shown in general by taking its expectation value, which we call the thermodynamic entropy, and noting that it rigorously satisfies the three laws of thermodynamics.

The rate of change of the thermodynamic entropy operator satisfies the equation

$$i \partial_t \hat{\mathcal{S}}_t = \mathcal{D} L \hat{\mathcal{S}}_t + \mathcal{D} L e^{-itNL} \mathcal{N} \hat{\mathcal{S}}_0 - i \int_0^t d\tau K_\tau \hat{\mathcal{S}}_{t-\tau}, \quad (34)$$

where $\mathcal{N} = 1 - \mathcal{D}$ projects operators to their nondiagonal parts, $L = [\hat{H}, \cdot]$ is the Liouville superoperator corresponding to \hat{H} , and $K_\tau = \mathcal{D} e^{-itNL} L \mathcal{N} L$ is known as the memory kernel. We use ∂_t in this section as a short-hand notation for $\partial/\partial t$.

For initial states of the local equilibrium form (which are diagonal) and for very weak coupling of the subsystems, the long-time evolution is Markovian, i.e., (34) becomes memoryless,

$$i \partial_t \hat{\mathcal{S}}_t = - \lim_{s \rightarrow 0^+} K_s \hat{\mathcal{S}}_t, \quad (35)$$

with K_s being the Laplace transform of K_τ . The expectation value of this equation leads to

$$\langle \partial_t \hat{\mathcal{S}}_t \rangle = \sum_{\alpha\alpha'} P_\alpha W_{\alpha\alpha'} \ln \frac{P_\alpha}{P_{\alpha'}}, \quad (36)$$

with the transition rates $W_{\alpha\alpha'} = 2\pi \delta(\varepsilon_\alpha - \varepsilon_{\alpha'}) |V_{\alpha\alpha'}|^2$, calculated in the lowest order in the coupling potential and $P_\alpha = \langle \alpha | \hat{\rho}_t | \alpha \rangle$ being the occupation probability of the state $|\alpha\rangle$ in its lowest-order approximation, satisfying the transport or Pauli master equation

$$\partial_t P_\alpha = \sum_{\alpha'} (P_{\alpha'} W_{\alpha'\alpha} - P_\alpha W_{\alpha\alpha'}). \quad (37)$$

Equation (36), which can alternatively be derived by writing the thermodynamic entropy in this approximation as

$$\langle \hat{\mathcal{S}}_t \rangle = - \sum_{\alpha} P_\alpha \ln P_\alpha, \quad (38)$$

differentiating and using (37), has the same form as the entropy production of an aged *classical* Markovian system with Gaussian fluctuations, where the α is in this case interpreted as a realization of the deviation of the thermodynamic (extensive) variables from their equilibrium values.

A special situation occurs when the coupling between subsystems is so weak that they can be treated as statistically uncorrelated as a first approximation. In this case, the thermodynamic entropy becomes additive, and an equation like (37) holds for the diagonal entries of the reduced density matrix of each subsystem.

Very weak coupling implies that equilibration within each subsystem takes places much faster than among them, and hence, if left alone, the long-time state of the system is one of local equilibrium, described by the factorized density matrix

$$\hat{\rho}^r = \bigotimes_l \hat{\rho}_l^r = \bigotimes_l \exp[-(\hat{\mathcal{H}}_l - \mu_l \hat{\mathcal{N}}_l - \Omega_l)/T_l], \quad (39)$$

with l labeling the different uncorrelated subsystems, with temperature T_l , chemical potential μ_l and thermodynamic potential $\Omega_l = \Omega_l(T_l, \mu_l, \{x_\lambda^l\})$; the latter is defined through the normalization of the density matrix, requiring $\text{Tr} \exp[-(\hat{\mathcal{H}}_l - \mu_l \hat{\mathcal{N}}_l)/T_l] = \exp(-\Omega_l/T_l)$.

The quantities $\{x_\lambda^l\}$ are a set of external parameters for subsystem l upon which its Hamiltonian $\hat{\mathcal{H}}_l$ depends; these parametrize the action of the operator which couples the degrees of freedom of the subsystem l to those of the other subsystems, and $\hat{\mathcal{N}}_l$ is the operator corresponding to the number of particles.

Since (39) is expressed in terms of (diagonal) thermodynamic operators, the thermodynamic entropy operator from (33) and (39) is

$$\hat{\mathcal{S}}^r = -\ln \hat{\rho}^r = \frac{1}{T_l} \sum_l (\hat{\mathcal{H}}_l - \mu_l \hat{\mathcal{N}}_l - \Omega_l). \quad (40)$$

The equation corresponding to (36) is easily shown to be the sum over all subsystems of the contributions $\langle d\hat{\mathcal{S}}_t^r \rangle$ obtained from

$$T_l \langle d\hat{\mathcal{S}}_t^r \rangle = \langle d\hat{\mathcal{H}}_l \rangle - \mu_l \langle d\hat{\mathcal{N}}_l \rangle + \sum_\lambda F_\lambda^l dx_\lambda^l, \quad (41)$$

where $F_\lambda^l = -\langle \partial \hat{\mathcal{H}}_l / \partial x_\lambda^l \rangle$. This may be written as the well-known form of the first law of thermodynamics

$$T_l \partial_t \langle \hat{\mathcal{S}}_t^r \rangle = \partial_t \langle \hat{\mathcal{H}}_l \rangle - \mu_l \partial_t \langle \hat{\mathcal{N}}_l \rangle + \sum_\lambda F_\lambda^l \partial_t x_\lambda^l, \quad (42)$$

provided the process takes place slowly enough, a condition which can be stated as $\|\partial_t \hat{\rho}^r\|$ being very small, in a norm defined in Ref. [13].

When the continuity equations for the local average energy and number of particles is used in (42), an expression for the total entropy production $\Pi = \partial_t \langle \hat{\mathcal{S}}^r \rangle$ in the system can then be obtained. This will be done for the particular case of two subsystems in contact in the following section.

B. Application to the one-atom maser

The dynamics of the Jaynes-Cummings model is special because, in the basis $\{|\alpha\rangle\} = \{|1, n+1\rangle, |2, n\rangle\}$, the diagonal entries of the reduced density matrices of each subsystem undergo Markovian evolution [as in (37)] independent of the strength of the coupling γ , as expressed by equations (24) and (26).

The very weak coupling condition enters the calculation of the thermodynamic entropy when correlations between the field and atoms are considered negligible to a first approximation so that (38) is additive among subsystems

$$S'_N = - \sum_i p'_i(N) \ln p'_i(N) - \sum_n P'_n(N) \ln P'_n(N). \quad (43)$$

After using the conservation of probabilities, we then have for the entropy production $\Pi'_N = dS'_N/dt$

$$\Pi'_N = - \sum_i \frac{dp'_i(N)}{dt} \ln p'_i(N) - \sum_n \frac{dP'_n(N)}{dt} \ln P'_n(N). \quad (44)$$

Since the state of the field is monitored through the atoms when these just leave the second cavity, we calculate (44) at time $t = \tau$ by using (24) and (26):

$$\Pi'_N = \left(\frac{\Omega}{T_a} - \frac{\omega}{T_{N+1}} \right) J_N^P, \quad (45)$$

where J_N^P is the photon current from the field to the N th atom when this is just leaving the second cavity,

$$J_N^P = \sum_n [P_{n+1}^0(N) w_{n+1,n} - P_n^0(N) w_{n,n+1}], \quad (46)$$

with the w evaluated at time $t = \tau$. In arriving at this result, we have used the fact that p_i^τ is initialized to $p_i^0 = \sigma_{ii}$, by construction, and that the state of the field each time a new atom enters the cavity can be assigned an effective temperature T_N :

$$P_{n+1}^0(N)/P_n^0(N) = e^{-\omega/T_N}. \quad (47)$$

This corresponds to the local equilibrium state discussed in (39) here evolving under a discrete dynamics: every time a new atom enters the cavity, both the atom and the photon field are thermal.

The discussion in the previous section then suggests that the entropy production calculated in (45) should be directly connected to that obtained using the arguments after (42). To this end, consider two classical subsystems which are in contact at temperatures T_1 and T_2 and respective chemical potentials μ_1 and μ_2 . The total entropy production Π for this system is

$$\Pi = \frac{1}{T_1} \frac{\delta Q_1}{dt} + \frac{1}{T_2} \frac{\delta Q_2}{dt}, \quad (48)$$

where δQ_i is the quantity of heat exchanged by the subsystem i with the other subsystem during a time interval dt , which is expressed at constant volume [constraints specified by the x_λ^i in (42) kept fixed] by

$$\delta Q_i = dE_i - \mu_i dN_i, \quad (49)$$

where E_i and N_i are, respectively, the average internal energy and number of particles of subsystem i . Using the conservation of energy and particles we have, in terms of the energy current J^E and a particle current J^P

$$J^E = \frac{dE_1}{dt} = -\frac{dE_2}{dt}, \quad J^P = \frac{dN_1}{dt} = -\frac{dN_2}{dt}. \quad (50)$$

Substituting (49) and (50) in (48), we can write the total entropy production as the sum $\Pi = \Pi^E + \Pi^P$ of the contributions from the two irreversible processes taking place: energy transport and particle diffusion, with the respective terms given by

$$\Pi = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) J^E + \left(\frac{\mu_2}{T_2} - \frac{\mu_1}{T_1} \right) J^P. \quad (51)$$

Thermodynamic equilibrium between the subsystems is characterized by the vanishing of the thermodynamic forces [quantities in parentheses in (51)] and the respective induced currents, and therefore of the total entropy production. This leads to the well-known conditions for equilibrium $T_1 = T_2$ and $\mu_1 = \mu_2$.

Having in mind these considerations, we observe that when the steady state of the field in the second cavity is approached,

$$P_n^0(N) \rightarrow \mathcal{P}_n \quad \therefore \quad T_N \rightarrow T_f. \quad (52)$$

By using (32) and the detailed balance condition (28) in (45) and (46), we then see that both the thermodynamic force [quantity in parentheses in (45)] and the induced current vanish in the steady state and hence the total entropy production. This shows that the steady state is a state of thermodynamic equilibrium.

An even more interesting insight is obtained when the nature of the transport processes with which equilibrium is approached in the second cavity is inquired. Since the particles being transported between the atoms and the field are photons, at resonance when $\omega = \Omega$ the energy current is $J^E = \omega J^P = \Omega J^P$, and then in (45) we have $\Pi'_N \rightarrow (1/T_a - 1/T_f) J^E$, which is of the form Π^E in (51). Out of resonance, when $\omega \neq \Omega$, we see instead that $\Pi'_N \rightarrow (\Omega/T_a - \omega/T_f) J^P$, which is of the form Π^P in (51), with $-\omega$ and $-\Omega$ playing the role of chemical potentials for the field and atoms, respectively.

We note that in obtaining the above description of the problem, we have pictured the dressed photons as having a chemical potential which is different (when $\omega \neq \Omega$) depending on whether these belong to the cavity field or to the atoms. A photon “belonging” to an atom is thought as absorbed by the atom, with the potential of giving it back to the field.

This identification of the chemical potential of the photons in the cavity, interacting with the atoms, requires abandoning the common belief that a vanishing chemical potential is a property of all photons (as in a black-body field), which is not generally so [15]. The chemical potential of radiation depends on the emitter and can even be positive if the latter has an energy gap through which the radiative transitions occur.

The remarks above therefore provide us with an interpretation of the results of the Jaynes-Cummings thought experiment. At resonance, energy transport is active when approaching the steady state and particle diffusion is absent (impermeable wall building up between the subsystems), a reason why the temperatures of the atoms and field equilibrate.

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Out of resonance only particle diffusion is active and energy transport is absent (adiabatic wall building up between the subsystems), and then the temperatures do not equilibrate.

The interference of different irreversible processes taking place in a thermodynamic system is basically a classical phenomenon formalized long ago by Onsager [16,17]. The fact that in the present situation, and under our interpretation, the processes become mutually exclusive depending on the detuning conditions of the cavity is a fully quantum-mechanical phenomenon: we are dealing with single atoms and photons.

V. CONCLUSION

By calculating the quantum entropy production in a system of atoms weakly interacting with a cavity field and comparing it to the classical results expected for a Markovian evolution, we have been able to infer the nature of the processes with which the steady state in a one-atom maser is approached both at resonance and out of resonance. In particular, we have shown that the lack of equilibration of temperatures of the subsystems in the off-resonant situation is consistent with the equilibrium state attained by two subsystems in contact but adiabatically insulated from each other. At resonance, this insulation is not present, and therefore the temperatures do equilibrate. The results presented here are representative of the new kind of information which can be gained by applying quantum-thermodynamic methods.

ACKNOWLEDGMENTS

I would like to acknowledge the support from the Fulbright-Colciencias Fellowship and the Columbia GSAS Faculty Fellowship, as well as helpful discussions with Prof. Andrew Millis, Junichi Okamoto and Zhouan He.

APPENDIX: THERMAL DISTRIBUTION OF THE PHOTON FIELD WHEN ATOMS ENTER THE CAVITY

The condition of weak coupling in (3) is fundamental for the present discussion since only in this case does a truly thermodynamic behavior correspond to the quantum statistics. This is actually realized in practice in cavity QED experiments in which $\gamma/\Omega \sim 10^{-7}$ is easily obtained [18], with very long decay times for the cavity $\tau_{\text{cav}}/\tau \sim 10^4$ and the atomic states $\tau_{\text{atom}}/\tau \sim 10^3$ [5].

We assume that it is impossible to have an infinite number of photons in the cavity at any time (e.g., that costs a lot if the photons have nonzero chemical potential) or, equivalently, that an integer M should exist such that, if there are n photons in the cavity, $n \leq M$. The weak very coupling condition can then be expressed as

$$0 < \gamma\tau \ll M^{-1}. \quad (\text{A1})$$

By expanding the transition probability $|b_n|$ evaluated at time τ in a power series in $\gamma\tau$ we then find, up to the leading order:

$$|b_n^\tau|^2 = (n+1)(\gamma\tau)^2. \quad (\text{A2})$$

If the probability distribution when the N th atom is entering the cavity is assumed to be thermal at temperature T_N we

should have

$$P_n^0(N) = a_N K_N^n, \quad K_N = e^{-\omega/T_N}, \quad (\text{A3})$$

where $a_N = 1 - K_N$ is the normalization constant. Note that the factor coming from the chemical potential μ is absorbed in the definition of a_N : $a_N \propto e^{\mu/T_N}$.

When (A3) is substituted in (20) at time τ we have

$$P_n^\tau(N) = a_N K_N^n \left[1 + K_N^{-1}(\sigma_{22} - K_N \sigma_{11}) \times (|b_{n-1}^\tau|^2 - K_N |b_n^\tau|^2) \right]. \quad (\text{A4})$$

The condition $P_n^\tau(N) = P_n^0(N+1)$ together with (A3) imply that we must have

$$a_{N+1} K_{N+1}^n = a_N K_N^n \left[1 + K_N^{-1}(\sigma_{22} - K_N \sigma_{11}) \times (|b_{n-1}^\tau|^2 - K_N |b_n^\tau|^2) \right]. \quad (\text{A5})$$

In order to satisfy this equation it is required that

$$e^{\frac{\omega(\Delta T_N/T_N)}{T_N + \Delta T_N}} (1 + X_N) = 1 + K_N^{-1}(\sigma_{22} - K_N \sigma_{11}) \times (|b_{n-1}^\tau|^2 - K_N |b_n^\tau|^2). \quad (\text{A6})$$

Replacing this in (A5) gives the recursive equations

$$a_{N+1} = (1 + X_N) a_N, \quad (\text{A7})$$

$$T_{N+1} = T_N + \Delta T_N. \quad (\text{A8})$$

The possibility of having a thermal distribution for the field every time a new atom enters the cavity then relies on the self-consistency of Eqs. (A7) and (A8).

Note that this description is symmetric with respect to making γ very small or instead making τ very small. In the latter case, it is not expected that the effective temperature of the field changes considerably after the passage of an atom and then $\Delta T_N/T_N \ll 1$.

Assuming $X_N \ll 1$ as well, we can then expand the left-hand side of (A6) and substitute (A2) in the right-hand side to obtain

$$(\omega/T_N)(\Delta T_N/T_N) = K_N^{-1}(\sigma_{22} - K_N \sigma_{11})(1 - K_N)(\gamma\tau)^2, \quad (\text{A9})$$

which determines the temperature changes at each step of the discrete dynamics, and

$$X_N = -(\sigma_{22} - K_N \sigma_{11})(\gamma\tau)^2, \quad (\text{A10})$$

which keeps the probability distribution of the photons normalized.

Using (A3) we have, in terms of the steady state temperature of the photon field $T_f = (\omega/\Omega) T_a$:

$$\Delta T_N/T_N = -\text{sech}\left(\frac{\omega}{2T_f}\right) \sinh\left[\frac{\omega}{2}\left(\frac{1}{T_f} - \frac{1}{T_N}\right)\right] \times \text{sinhc}\left(\frac{\omega}{2T_N}\right)(\gamma\tau)^2. \quad (\text{A11})$$

This proves the consistency of (A8) since, beginning with a temperature $T_i = T_{N=1}$ for the field, if $T_i > T_f$, (A11) says that the field will start cooling as atoms cross the cavity until

the temperature of the steady state T_f is reached after which no more temperature changes occur. Heating of the field will happen instead if $T_i < T_f$.

It should be mentioned, as seen from (A11), that if $\omega/T_f < 1$ the cooling process can take place from any initial temperature $T_i > T_f$. However, the heating process can not start from arbitrarily low temperatures since the prefactor of $(\gamma\tau)^2$ in (A11) can grow arbitrarily, with the possibility of making $\Delta T_N/T_N \ll 1$ inconsistent. The same reasoning applied to the case $\omega/T_f > 1$ shows that cooling consistently takes place only for sufficiently large initial temperatures.

These observations are in line with the third law of thermodynamics, which, in one of its forms, states that the specific heat of materials tend to zero as the temperature goes to zero or, in other words, it is very hard to change the temperature when the system is close to the absolute zero.

We now turn our attention to the consistency of (A7). This is proven by rewriting that equation, on one hand, in terms of $a_N = 1 - K_N$ and using (A10)

$$K_{N+1} = K_N + (\sigma_{22} - K_N\sigma_{11})(1 - K_N)(\gamma\tau)^2. \quad (\text{A12})$$

On the other hand, by expanding K_{N+1} in a Taylor series about $\Delta T_N/T_N = 0$ we easily get, up to leading order,

$$K_{N+1} = K_N + K_N(\omega/T_N)(\Delta T_N/T_N), \quad (\text{A13})$$

which, after using (A9), is equivalent to (A12).

We have therefore proven the consistency of both (A7) and (A8) and then the probability distribution of the field every time a new atom enters the cavity is really thermal in the weak coupling limit.

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