Quantum Thermodynamics Lecture Notes

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I. WEAK-COUPLING FORMULATION OF QUANTUM THERMODYNAMICS

Thermodynamics, whether its phenomenological formulation or its statistical one, is a theory for large systems. It is all about emergent properties of systems when coarse-graining is a fundamental part of the observation process, be those systems isolated or in contact with other bodies. Through a quantum mechanical description, however, one is in general able to describe the physics of the tiniest of objects. In these types of studies there is no coarse-graining involved; for a closed quantum system, the dynamics is exactly known through Schrödinger's evolution and there are no emergent properties. This motivates the need for considering open quantum systems as typical situations in which to study phenomenons of thermodynamics in the quantum regime: the emergent properties arise from tracing out the environment, which constitutes a form of coarse graining.

The theory of open systems therefore represents the technical toolbox through which one may attempt a formulation of quantum thermodynamics. The point of view for the theory is inherently a dynamical one, concerned mostly with the change of thermodynamic properties as the system evolves in time. As a consequence, it is also mainly concerned with nonequilibrium scenarios.

In these notes on the theory of nonequilibrium quantum thermodynamics, we review the fundamentals of its most accepted formulation, namely the one based on the assumption that the system's coupling with the environment is weak. This framework was set up mostly in the end of the seventies by Alicki, Spohn and Lebowitz [1–3]. The ideas are simple, and rely on the Markovian evolution of the open system of interest. As will be shown, the unique characterization of the thermodynamic quantities also heavily relies on the possibility of neglecting the interaction energy contribution in several different ways. Reviews and material on this topic include [4, 5].

A. Internal energy, heat and work and the first law

The first assumption of the theory on nonequilibrium quantum thermodynamics is identical to that of open system theory: we consider a closed system — typically a part of the universe or, at most, the whole universe itself — which does not interact with anything else and whose evolution is given by a unitary transformation. Of this system, we are interested in a specific subsystem S which then interacts with the rest, the environment E. The dynamics of the reduced system S is provided by tools of open system theory. The theory of quantum thermodynamics is then interested in the thermodynamic properties of the subsystem S as it evolves with the environment. These properties therefore strictly depend on the dynamics of S and thus describe nonequilibrium processes. In typical weak-coupling quantum thermodynamics, the environment is assumed to be large and in a thermal state; thus, similar to open system theory, it is standard to assume that system and environment start uncorrelated, i.e. $\rho_{SE}(0) = \rho_S(0) \otimes \rho_E(0)$ with $\rho_E(0)$ in a Gibbs state of the environmental Hamiltonian at a certain temperature.

The second assumption is that system and environment are weakly interacting. In the literature, it is not always specified what "weakly interacting" formally means. A consistent derivation of the theory, though, relies on this definition. In the following, we assume that "weakly interacting", from a dynamical point of view, means that the dynamics of the system S is governed by a master equation with a dissipator in Lindblad form and with the unitary part given by a commutator with the bare system Hamiltonian $H_S(t)$. Then, properties of the dynamics are well understood; the question, now, is how to correctly define thermodynamic quantities associated to S.

Assume that the total Hamiltonian is given by three parts, describing the system, the environment, and their interaction respectively:

$$H_{SE}(t) = H_S(t) + H_E + \lambda H_I(t) \ . \tag{1}$$

Notice that we specifically allow both the system and the interaction Hamiltonian to depend on time. This indicates some external control over the system degrees of freedom, which can change in time due to an external agent performing some protocol on it in a way that doesn't affect the unitarity of the evolution of the system-environment universe. It also indicates some control over the interaction; in particular we allow for protocols turning the interaction on or off, be them rapid or fully adiabatic. The environmental Hamiltonian is instead assumed to be time independent, in agreement with the assumption that the environment is somehow too large and complex to be controlled. Moreover, we have made explicit a parameter λ in the interaction Hamiltonian, which acts as a coupling parameter and tunes the strength of the interaction. In quantum thermodynamics, this parameter is taken to be small with respect to main parameters in the system and in the environment so that the two are effectively weakly interacting.

The entire system is a closed, typically large statistical system whose internal energy can be simply identified with the expectation value of the Hamiltonian (1):

$$U_{SE}(t) = \langle H_{SE}(t)\rangle_t = \langle H_S(t)\rangle_t + \langle H_E\rangle_t + \lambda\langle H_I(t)\rangle_t \; . \tag{2}$$

We can now give an additional condition which, from an energetic point of view, takes part in the assumption that system and environment are weakly interacting, namely that the contribution to the total internal energy $U_{SE}(t)$ coming from the interaction is negligible

$$U_{SE}(t) \approx \langle H_S(t)\rangle_t + \langle H_E\rangle_t \; . \tag{3}$$

From this one obtains a natural definition for the internal energy of the open system S simply as the expectation value of its bare Hamiltonian,

$$U_S(t) := \langle H_S(t)\rangle_t \; , \tag{4}$$

and analogously for the environment, $U_E(t) := \langle H_E\rangle_t$, with the consequence that, in the weak coupling regime, the internal energy is additive, just like in macroscopic thermodynamic systems. The given definition of internal energy is also compatible with the statistical formulation of thermodynamic internal energy for many-particle classical systems — e.g., a gas in a box — where the interaction with the external environment is typically modelled via short-range interactions at the system's boundaries.

The comparison with quantities of the total closed system also helps to give a reasonable definition for work done on (or by) the system S. Since the total system is closed, there can be no heat exchange with anything else; therefore the total energy change can only be given by work, i.e.

$$\Delta U_{SE}(t) = \delta W_{SE}(t) \; , \tag{5}$$

where $\Delta U_{SE} = U_{SE}(t) - U_{SE}(0)$ denotes the two-point internal energy change in time, and the work exchanged during the process is denoted with δW_{SE} to highlight the fact that its value typically depends on the evolution between the two points in time — a consequence of work exchange not being given by an exact differential in general. Making use of the unitarity of the total evolution and of the fact that the environment Hamiltonian is time independent, we can rewrite the work contribution as

$$\delta W_{SE}(t) = \int_0^t \mathrm{d}\tau \mathrm{Tr}_S\{\dot{H}_S(\tau)\rho_S(\tau)\} + \lambda \int_0^t \mathrm{d}\tau \mathrm{Tr}\{\dot{H}_I(\tau)\rho_{SE}(\tau)\} \; . \tag{6}$$

By again neglecting the interaction contribution, we conclude that the work on the total system is given by the explicit dependence of H_S on time, and depends only on the degrees of freedom of S. Therefore, we identify the work done on (or by) the system from time 0 to time t as

$$\delta W_S(t) := \int_0^t \mathrm{d}\tau \mathrm{Tr}\{\dot{H}_S(\tau)\rho_S(\tau)\} \; . \tag{7}$$

Specifically, work arises from explicit time-dependencies of the Hamiltonian. This is again compatible with the statistical formulation of classical thermodynamics in nonequilibrium processes.

The immediate consequence of applying an analogue expression to the environmental degrees of freedom is that there is never any work done on, or by, the environment:

$$\delta W_E(t) := \int_0^t \mathrm{d}\tau \mathrm{Tr}\{\dot{H}_E(\tau)\rho_E(\tau)\} \equiv 0 \ . \tag{8}$$

Now that we have a definition for internal energy and work of the open system S, we can state a first law of quantum thermodynamics

$$\Delta U_S(t) = \delta W_S(t) + \delta Q_S(t) \ , \tag{9}$$

by defining the heat exchange contribution for the system as

$$\delta Q_S(t) := \int_0^t \mathrm{d}\tau \mathrm{Tr}\{H_S(\tau)\dot{\rho}_S(\tau)\} \ . \tag{10}$$

Thus, while work is associated to energy change due to the change of an external parameter in the Hamiltonian, heat is associated to the energy change due to the change in the system's statistics and populations. Furthermore, assuming that the system's evolution is governed by a Lindblad master equation with a negligible Lamb shift, namely $\dot{\rho}_S(t) = -i[H_S(t), \rho_S(t)] + \mathcal{D}[\rho_S(t)]$, we find that the heat exchange arises from the dissipative part of the system evolution

$$\delta Q_S(t) = \int_0^t \mathrm{d}\tau \mathrm{Tr}\{H_S(\tau)\mathcal{D}[\rho_S(\tau)]\} \ . \tag{11}$$

Looking again at total system quantities, we verify that under this definition of heat the total system heat exchange is indeed zero due to the unitarity of the evolution:

$$\delta Q_{SE}(t) = \int_0^t \mathrm{d}\tau \mathrm{Tr}\{H_{SE}(\tau)\dot{\rho}_{SE}(\tau)\} \equiv 0 \ . \tag{12}$$

Then, analogously defining a heat exchange contribution for the environment

$$\delta Q_E(t) := \int_0^t \mathrm{d}\tau \mathrm{Tr}\{H_E(\tau)\dot{\rho}_E(\tau)\} \tag{13}$$

and neglecting contributions from the interaction Hamiltonian in the total heat exchange $\delta Q_{SE}(t)$, we find that for weakly coupled systems the usual relation holds,

$$\delta Q_S(t) = -\delta Q_E(t) \ , \tag{14}$$

stating that any heat flowing out of the system at any point in time is entering the environment — and vice versa — in complete agreement with macroscopic thermodynamics. In the next section we will see how this definition of heat is used in a definition for the open system's entropy production, and how this leads to a formulation for the second law of themodynamics in the weak coupling regime.

B. Entropy production and the second law

With the definitions for the different types of energies established in the previous section, we can now look at entropic properties of an open quantum system and see how the second law of thermodynamics looks in this scenario. This mainly takes the form of positivity of entropy production rate, and was established by the seminal work of Spohn and Lebowitz in 1978 [1, 2].

1. *Positive entropy production*

First of all, let us assume that the system Hamiltonian is time independent, $H_S(t) \equiv H_S$. We further assume that the open system evolution is described by a semigroup of CP dynamical maps Φ_t which admits the Gibbs state as a stationary state, i.e.

$$\Phi_t\left[\frac{e^{-\beta H_S}}{Z_S}\right] = \frac{e^{-\beta H_S}}{Z_S} \quad \text{or} \quad \mathcal{L}\left[\frac{e^{-\beta H_S}}{Z_S}\right] = 0 \;, \tag{15}$$

with $\mathcal{L}$ the Lindblad generator of the quantum dynamical semigroup. The above is satisfied, for example, for the Lindblad generator derived microscopically through a Born-Markov approximation, if we assume that the environment is initially in a Gibbs state at inverse temperature β. Then we may define entropy production for an open system in complete analogy to Clausius' inequality for macroscopic systems. Namely, we write the entropy production for a nonequilibrium quantum process as

$$\Sigma_S(t) = \Delta S_S(t) - \beta \delta Q_S(t) \;, \tag{16}$$

where $\Delta S_S(t)$ is the change in the von Neumann entropy of the system

$$S_S(t) = -\mathrm{Tr}\{\rho_S(t) \ln \rho_S(t)\} \;, \tag{17}$$

while $\delta Q_S(t)$ is given by (11). By taking the time derivative of $\Sigma_S(t)$, we can write the entropy production rate as

$$\sigma_S(t) := \dot{\Sigma}_S(t) = \frac{\mathrm{d}}{\mathrm{d}t} S_S(t) + J_S(t) \;, \tag{18}$$

where J_S denotes the entropy flux from the open system to the environment. This is given by

$$\begin{aligned} J_S(t) &= -\beta \dot{Q}_S(t) = -\beta \mathrm{Tr}\{H_S \mathcal{L}[\rho_S(t)]\} \\ &= \mathrm{Tr}\{\mathcal{L}[\rho_S(t)] \ln \rho_S^G\} \;, \end{aligned} \tag{19}$$

where we used ρ_S^G to denote the Gibbs state, while the derivative of the von Neumann entropy gives

$$\frac{\mathrm{d}}{\mathrm{d}t} S_S(t) = -\mathrm{Tr}\{\mathcal{L}[\rho_S(t)] \ln \rho_S(t)\} \;. \tag{20}$$

These contributions lead to the following expression for entropy production in terms of relative entropy between the system state and the Gibbs state:

$$\sigma_S(t) = -\frac{\mathrm{d}}{\mathrm{d}t} S(\rho_S(t) || \rho_S^G) \;. \tag{21}$$

With this one proves the following theorem:

Theorem 1. *For an open system evolving under a CP dynamical semigroup of generator $\mathcal{L}$ for which the Gibbs state $\rho_S^G = e^{-\beta H_S}/Z_S$ is a stationary state, the entropy production rate* (21) *is positive*

$$\sigma_S(t) \geq 0 \;, \tag{22}$$

and vanishes when the system enters a stationary state $\mathcal{L}[\rho_S(t)] = 0$. Moreover, the equality sign holds at all times for a completely reversible process $\mathcal{L} = -i[H_S, \cdot]$.

Proof. Recalling that the relative entropy is contracting under the simultaneous application of a completely positive dynamical map Φ_t to both arguments, we find

$$\begin{aligned} S(\rho_S(t) || \rho_S^G) &= S(\Phi_t[\rho_S(0)] || \Phi_t[\rho_S^G]) \\ &\leq S(\rho_S(0) || \rho_S^G) \;. \end{aligned} \tag{23}$$

Since the maps Φ_t form a completely positive semigroup, it follows that the relative entropy above decreases monotonically and therefore

$$\frac{\mathrm{d}}{\mathrm{d}t} S(\rho_S(t)||\rho_S^G) \leq 0 \; , \tag{24}$$

which grants the positivity of $\sigma_S(t)$. The last statements can be inferred easily from expressions (19) and (20), and from the invariance of relative entropy under unitary transformations. □

Theorem 1 is understood and accepted to be an expression for the second law of quantum thermodynamics at weak coupling. It states that, whenever we have a system S weakly coupled to an environment E — initially in an equilibrium state and uncorrelated with S — obeying a Markovian semi-group evolution, the entropy production rate is always positive, showing a continuous increase in the entropy production Σ, thus implying that the evolution is a completely irreversible process for the system S. Furthermore, if the system is ergodic — namely the only conserved quantity for the system is the identity operator — then the system is completely relaxing to the unique steady state given by the Gibbs state [6]. This proves and provides the conditions for approach to equilibrium in a weakly coupled open system S.

II. THE OTTO CYCLE

One of the more practical and application-oriented goals of quantum thermodynamics is the development of quantum analogues of heat engine and thermal cycles. Since the short note by Scovil and Schulz-DuBois appearing in Physical Review Letters in 1959 [7] — barely more than one page long — which theoretized the possible use of three-level masers as quantum heat engines, the study of this kind of applications has received great attention and interest, powered by the tangible possibility of experimental realizations of such devices. In recent years, such machines have been indeed realized experimentally [8–13].

A paradigmatic model of a quantum heat engine is given by a quantum analogue of the Otto cycle, studied within the framework of weak-coupling non-equilibrium quantum thermodynamics. As its macroscopic version, it consist of four phases (compression/expansion and heating/cooling). This kind of heat engine can operate for small quantum system such as few-level system or for a single quantum harmonic oscillator.

The quantum Otto cycle with a harmonic oscillator as working system is a four-stroke cycle where the harmonic oscillator undergoes two phases of adiabatic driving of its frequency (compression and expansion), alternated by two isochoric phases (heating and cooling) where no driving occurs, and where the environment is a large thermal bath at a certain temperature and couples weakly to the system.

We write the bare Hamiltonian of the system in ladder operator notation, namely $H_S = \omega_1 a^\dagger a$, and assume that any driving imposed during the cycle is adiabatic such that the time-dependency of the protocol appears only in the explicit frequency of H_S, while a and $a^\dagger$ are effectively frequency independent. In the literature, this kind of driving is referred to as having an adiabaticity parameter Q^* equal to 1 [14, 15]. The four phases of the Markovian quantum Otto cycle are described as follows [16]:

1. **Phase I: Adiabatic compression** — in this first phase, taking place from time t_0 to time t_1 (assume time is "reset" to t_0 at every new start of the cycle) the frequency of the harmonic oscillator is ramped up from its bare frequency ω_1 to a final value $\omega_2 > \omega_1$, through a protocol which is assumed to be adiabatic and frictionless, namely completely reversible and described by a unitary transformation generated by the Hamiltonian

   $$H_S(t) = \omega(t) a^\dagger a \; . \tag{25}$$

   The exact form of the driving protocol is left unspecified, as the only requirement necessary is that it is slow enough and that it leads to the required final frequency — thus, we impose $\omega(t_0) \equiv \omega_1$ and $\omega(t_1) \equiv \omega_2$.

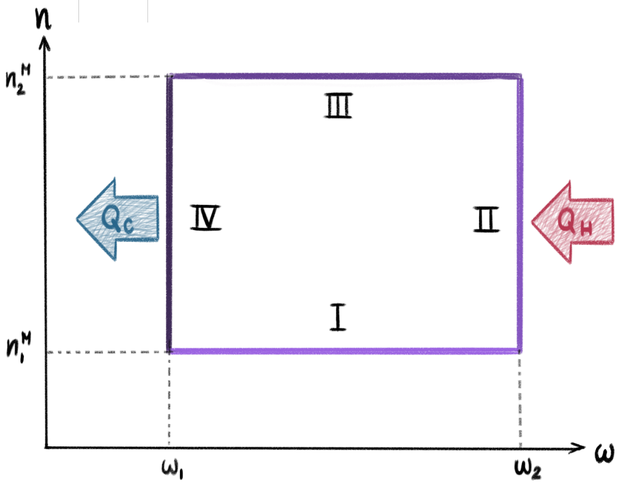

Figure 1. Sketch of the Otto cycle in the $n-\omega$ plane.

Because the driven system is effectively a closed driven system, there is no heat exchange during this phase, and the mean occupation number $n(t) = \langle a^\dagger a \rangle_t$ of the oscillator is naturally a conserved quantity. We assume that the system is prepared at t_0 in a thermal equilibrium state of temperature T_1; this is left invariant in this phase and is determined by

$$n_1^{\mathrm{M}} = \frac{1}{e^{\omega_1/T_1} - 1} \,, \tag{26}$$

where the superscript M is used to denote that the quantities we are treating refer to the Markovian cycle — as opposed of what will be treated in the next section. Then, the internal energy change — and, consequently, the work exchanged — during this phase is determined by the initial mean occupation number and by the frequency difference, namely

$$W_{\mathrm{I}} = (\omega_2 - \omega_1) n_1^{\mathrm{M}}, \qquad Q_{\mathrm{I}} = 0. \tag{27}$$

2. **Phase II: Isochoric heating** — in this phase, the frequency of the oscillator is kept fixed at ω_2, while the system is connected to a hot bath at temperature $T_2 > T_1$. The evolution of the oscillator whilst coupled to the bath is modelled through a Lindblad (Born-Markov) master equation that leads to open system equilibrium at long times. We assume that this phase lasts until a certain time t_2 which is taken long enough for thermalization to occur in the system; thus, the final state here is again a Gibbs state of the oscillator, but this time with respect to frequency ω_2 and temperature T_2, namely described by the mean occupation number

$$n_2^{\mathrm{M}} = \frac{1}{e^{\omega_2/T_2} - 1} \,. \tag{28}$$

Note that the steady state does not depend on the initial state of the system, but only on the temperature of the bath T_2 and on the frequency ω_2. Since there is no driving protocol in this phase, the work exchanged is zero, while the heat exchanged corresponds to the change in the system's internal energy, namely

$$W_{\mathrm{II}} = 0, \qquad Q_H = Q_{\mathrm{II}} = \omega_2 (n_2^{\mathrm{M}} - n_1^{\mathrm{M}}) \,. \tag{29}$$

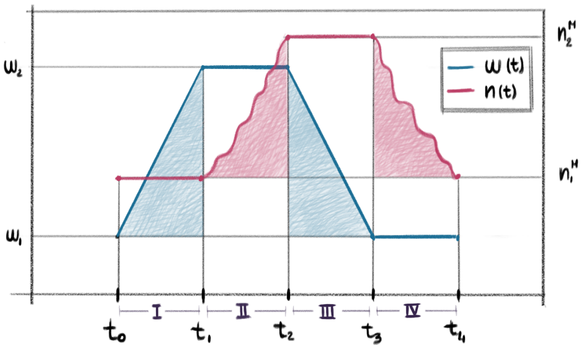

Figure 2. Qualitative sketch of the variation of frequency and average excitation number of the central harmonic oscillator through the phases of the Markovian Otto cycle.

3. **Phase III: Adiabatic expansion** — in this phase, mirror of phase I, the oscillator is disconnected from the bath while its frequency is driven down to its initial value ω_1 at a final time t_3. Therefore we have again an evolution according to unitary dynamics with Hamiltonian (25), where the driving protocol is still adiabatic but this time such that $\omega(t_2) \equiv \omega_2$ and $\omega(t_3) \equiv \omega_1$. As in phase I, the occupation number remains constant at the value n_2^{M}, leading again to zero heat exchange and to a work depending only on the two frequencies and the initial n, namely

$$W_{\mathrm{III}} = (\omega_1 - \omega_2) n_2^{\mathrm{M}}, \qquad Q_{\mathrm{III}} = 0 \ . \tag{30}$$

4. **Phase IV: Isochoric cooling** — in the last phase, similar to phase II, the frequency driving is interrupted and the oscillator is connected again to a thermal bath such that the oscillator is reaching thermalization once more at time t_4 long enough. This is a cooling phase, as the temperature T_1 of the bath is chosen identical to the one which the oscillator was initialized in at the beginning of phase I, and thus the bath is cold with respect to the one employed in phase II; furthermore, this choice closes the cycle as the final state and energy of the system match the ones at the beginning of the cycle. Just as in phase II, there is no work exchange during this phase, while heat depends on the static frequency ω_1 and on the different temperatures:

$$W_{\mathrm{IV}} = 0, \qquad Q_{\mathrm{IV}} = \omega_1 (n_1^{\mathrm{M}} - n_2^{\mathrm{M}}) \ . \tag{31}$$

To summarize the thermodynamic properties of the four phases, let us notice that since the Hamiltonian for the system in the weak-coupling limit is of the form $H_S(t) = \omega(t) a^\dagger a$ during the whole cycle, we can simply write, for any work and heat exchanged from a time t_i to a time t_f:

$$W = \int_{t_i}^{t_f} d\tau \dot{\omega}(\tau) n(\tau), \qquad Q = \int_{t_i}^{t_f} d\tau \omega(\tau) \dot{n}(\tau) \ . \tag{32}$$

Then, a non-zero work rate exists only at those times where $\omega(t)$ is varying, while a heat rate exists only for varying mean occupation number $n(t)$. We qualitatively sketch the behaviour of these two quantities during the entire cycle in Fig. 2. Since at each phase either one of the two quantities is constant, either work or heat are zero in each phase, as we saw above; consequently, we can calculate the other thermodynamic quantity simply by internal energy variation. If both $\omega(t)$ and $n(t)$ were to vary at the same time, as will be the case later, we would need to integrate in the time interval according to (32).

Now that we have assessed the value of the relevant thermodynamic quantities during the cycle, we can evaluate its efficiency. The relevant "gain" quantity of the cycle is the total work output $W_{\rm out} := -(W_{\rm I} + W_{\rm II} + W_{\rm III} + W_{\rm IV})$, which according to eqs. (27)-(31) reads

$$W_{\rm out} = -(W_{\rm I} + W_{\rm III}) = (\omega_2 - \omega_1)(n_2^{\rm M} - n_1^{\rm M}) \ . \tag{33}$$

The cycle is "operating" only when $W_{\rm out} > 0$, i.e. work is produced by the cycle. This condition according to the above is equivalent to imposing $T_1/T_2 < \omega_1/\omega_2$. If the total work output is negative, then we define the efficiency to be zero, as the cycle is not performing as wished. Instead, if $W_{\rm out} > 0$, the thermodynamic efficiency η of the cycle is traditionally defined as the ratio between the total work output $W_{\rm out}$ and the heat input $Q_H := Q_{\rm II}$ from the hot bath, namely

$$\eta^{\rm M} = \begin{cases} \frac{W_{\rm out}}{Q_H} = 1 - \frac{\omega_1}{\omega_2} \quad \text{if} \quad \frac{T_1}{T_2} < \frac{\omega_1}{\omega_2} \\ 0 \quad \text{if} \quad \frac{T_1}{T_2} \geq \frac{\omega_1}{\omega_2} \end{cases} . \tag{34}$$

From the requirement of an operating engine we can also find the Carnot upper bound to the efficiency, namely

$$\eta^{\rm M} \leq \eta^{\rm C} = 1 - \frac{T_1}{T_2} \ . \tag{35}$$

The results obtained for the Otto cycle, assuming a Born-Markov evolution for the phases where the system is in contact with the bath, are therefore formally equivalent to the ones obtained for the corresponding macroscopic engine. This is because the main assumptions are indeed the same: an adiabatic change of volume that does not perturb the equilibrium state of the system, and a thermalization process leading to thermal equilibrium at the same temperature of the bath.

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