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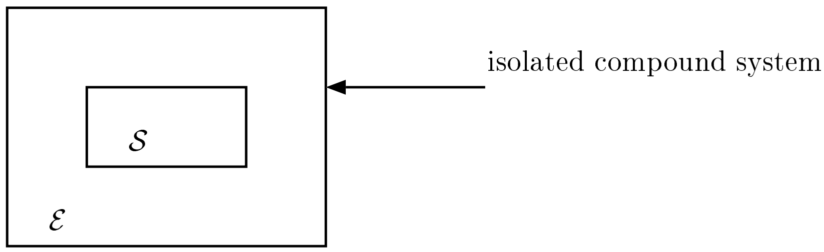
DYNAMICS IN QUANTUM THERMODYNAMICS

Abstract. A thermodynamical system being in contact with its environment is investigated by use of quantum-thermodynamical description. Since the considered system can only described by a restricted set of relevant observables, it performs an irreversible non-equilibrium process. Different statistical operators accompanying the non-equilibrium process are investigated, if their dynamics determine the expectation values of the set-variables correctly in time. The positivity of the entropy production of one of the dynamics is discussed.

1. Introduction

Thermodynamics is the theory of non-equilibrium systems. The main problem that arises, if we want a quantum mechanical description of thermodynamics, is how to get irreversibility into the reversible theory of quantum dynamics in order to get a positive entropy production. One possibility is to introduce dissipative terms into SCHRÖDINGER's equation or into the VON NEUMANN dynamics. This leads to an irreversible quantum theory (see for instance [1]). An other possibility is this mesoscopic description of a thermodynamic system using only its restricted macroscopic information with respect to the observables. The microscopic background theory remains unchanged (see for instance [2], [3]). There is also a combination of these two methods treated in [4], [5]. We will use here the second one of the above-mentioned methods, the mesoscopic theory using conventional microscopic dynamics.

Let us consider a discrete system $\mathcal{S}$. The interaction between $\mathcal{S}$ and its environment shall be completely described by their heat exchange, power exchange and material exchange. Such systems are called SCHOTTKY systems according to [6]. Let $\mathcal{S}$ be included in an isolated system, so that we can call that part of the isolated system, that is not $\mathcal{S}$, the environment $\mathcal{E}$.



Since the isolated compound system does not interact with any environment, we can choose a quantum mechanical description using its density matrix satisfying the VON NEUMANN dynamics.

The mesoscopic description of $\mathcal{S}$ is based on the choise of a restricted set of observables

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that are relevant to the considered problem. This set of relevant observables which have to be linearily independent of each other is called *beobachtungsebene* [7]

$$\mathcal{B} := \{G_1, \dots, G_n\}$$

$$G_i = G_i^+ \quad \textit{for all } \; i \in \{1, \dots, n\}\,.$$

Let us introduce the abbreviation

$$\mathbf{G} := (G_1 \dots G_n)^t\,.$$

The expectation values of those observables are given by

$$\begin{array}{rrcl} & g_i & := & \mathrm{tr}\,(G_i\,\varrho) \quad \textit{for all } \; i \in \{1, \dots, n\} \\ \text{or} & \mathbf{g} & := & \mathrm{tr}\,(\mathbf{G}\,\varrho)\,, \end{array}$$

if ϱ is the microscopic density operator of the considered isolated compound system.

In the standard situation, the observables $\mathbf{G}$ of the beobachtungsebene depend on some work variables $a_1(t), \dots, a_m(t)$. This is for instance the case, if we vary the volume of the considered discrete system $\mathcal{S}$ with a piston during the experiment. The abbreviation

$$\mathbf{a} := (a_1 \dots a_m)^T$$

will be used henceforth.

On the mesoscopic level of description we are not interested in the exact microscopic state ϱ, but in the expectation values $\mathbf{g} = \mathrm{tr}\,(\mathbf{G}\,\varrho)$ of the observables which we are able to measure. For a chosen set of observables $\mathbf{G}(\mathbf{a})$, there exist a lot of microscopical states that are macroscopically indistinguishable, because their expectation values $\mathbf{g}$ are the same. In this context, we can define:

A density operator $\hat{\varrho}$ is called *accompanying process of ϱ with respect to $\mathcal{B}$*, if

$$\mathrm{tr}\left(\mathbf{G}(t)\,\varrho(t)\right) = \mathrm{tr}\left(\mathbf{G}(t)\,\hat{\varrho}(t)\right)$$

$$\mathrm{tr}\,\hat{\varrho}(t) = 1 \qquad \mathrm{tr}\,\dot{\hat{\varrho}}(t) = 0 \qquad \text{for } t \in \mathbb{R}.$$

We are now free to choose any of the accompanying processes for describing the original process.

2. Dynamics of accompanying processes

2.1. Canonical dynamics

The accompanying process $\hat{\varrho}$ of ϱ with respect to $\mathcal{B}$ that maximalizes the entropy of the considered system will be denoted as R:

(1) $$S_{\mathcal{B}} := -k \min_{\hat{\varrho}} (\mathrm{tr}\,(\hat{\varrho}\;\ln \hat{\varrho})) = -k\,\mathrm{tr}\,(R\;\ln R)\,.$$

Here k is the BOLTZMAN constant. R has the following form [8] [9]:

(2) $$R = \frac{1}{Z}\,e^{-\lambda\cdot\mathbf{G}}$$

with the partition function

(3) $$Z := \mathrm{tr}\;e^{-\lambda\cdot\mathbf{G}}\,.$$

R is called *generalized canonical operator* (with respect to $\mathcal{B}$). The λ are called Lagrangian multipliers. Dynamics which preserve the canonical form of the density operator of maximal entropy for all times are called *canonical*.

From (2) and (3) we can see that the generalized canonical operator depends on the λ and the $\mathbf{G}(\mathbf{a})$. Thus we can derive the canonical dynamics as follows:

$$\dot{R} = \frac{\partial R}{\partial \mathbf{a}} \cdot \dot{\mathbf{a}} + \frac{\partial R}{\partial \lambda} \cdot \dot{\lambda}\,,$$

and the coefficients are calculated in [2]. Inserting them we can state:

Canonical dynamics is given by

$$\dot{R} = R\,\lambda \cdot \left(\mathrm{tr}\left(R\,\frac{\partial \mathbf{G}}{\partial \mathbf{a}} \right) - \frac{\partial \mathbb{G}}{\partial \mathbb{A}} \right) \cdot \dot{\mathbf{a}} + R\left(\mathrm{tr}\,(R\,\mathbf{G}) - \mathbb{G} \right) \cdot \dot{\lambda}$$

with

$$\begin{aligned} \mathbb{G} \quad &:= \quad \int_0^1 e^{\mu\lambda\cdot\mathbf{G}}\,\mathbf{G}\,e^{-\mu\lambda\cdot\mathbf{G}}\,d\mu \\ \frac{\partial \mathbb{G}}{\partial \mathbb{A}} \quad &:= \quad \int_0^1 e^{\mu\lambda\cdot\mathbf{G}}\,\frac{\partial \mathbf{G}}{\partial \mathbf{a}}\,e^{-\mu\lambda\cdot\mathbf{G}}\,d\mu\,. \end{aligned}$$

2.2. The relevant part of the density operator

The vector space of linear operators on HILBERT space is called LIOUVILLE space $\mathcal{L}$ [10]. For instance the density matrix and the observables are elements of this space. Now we can introduce linear mappings on $\mathcal{L}$, so-called super-operators. An example of a super-operator is the LIOUVILLE operator (5). Here super-operators are interesting which enable us to derive dynamics of the generalized canonical operator.

Since the operators in a chosen beobachtungsebene do not form a complete base in the LIOUVILLE space $\mathcal{L}$, the density matrix has for this particular beobachtungsebene a relevant part, which contributes to the calculation of expectation values, and an irrelevant part, which does not show any effect on the trace in the expectation values:

$$\varrho(t) = \varrho_{rel}(t) + \varrho_{irrel}(t)$$

with

$$\begin{aligned} \mathrm{tr}\left(\mathbf{G}(t)\,\varrho(t)\right) \quad &= \quad \mathrm{tr}\left(\mathbf{G}(t)\,\varrho_{rel}(t)\right), \\ \mathbf{0} \quad &= \quad \mathrm{tr}\left(\mathbf{G}(t)\,\varrho_{irrel}(t)\right) \end{aligned}$$

$$\mathrm{tr}\,\varrho_{rel}(t) = 1 \quad , \quad \mathrm{tr}\,\dot{\varrho}_{rel}(t) = 0\,.$$

The isolation of these two parts is achieved by a linear mapping on $\mathcal{L}$. This operator transforms the VON NEUMANN equation – the quantum-mechanical dynamics of the density operator in SCHRÖDINGER's picture

$$\dot{\varrho}(t) = -i L\,\varrho(t) \tag{4}$$

– into a mesoscopic dynamics of the generalized canonical operator. Here, L is the LIOUVILLE operator

$$L\,X := \frac{1}{\hbar}\,[\mathcal{H}, X]\,. \tag{5}$$

(For more detailed information about the relevant/irrelevant part of ϱ see [11].)

There are two different methods to isolate the relevant part of the microscopic density operator. This mapping can be either linear or local linear.

1. relevant part by a *linear* mapping

$$\varrho_{rel}(t) = P(t)\,\varrho(t)\,, \tag{6}$$

2. relevant part by a *local linear* mapping

$$\dot{\varrho}_{rel}(t) = P(t)\,\dot{\varrho}(t)\,. \tag{7}$$

Here, $P(t)$ is supposed to be an idempotent super-operator, because it is desirable that

$$P(t)\,\varrho_{rel}(t) = \varrho_{rel}(t)$$

or

$$P(t)\,\dot{\varrho}_{rel}(t) = \dot{\varrho}_{rel}(t)$$

is valid. Let us define the operator

$$Q(t) := \underline{\underline{1}} - P(t)\,.$$

If P is idempotent, Q is idempotent, too.

We can also project an accompanying process instead of the microscopic density operator. Both procedures should yield the same relevant part, because both $\hat{\varrho}$ and ϱ describe the same macroscopic state and yield the same expectation values.

$$P(t)\,\varrho(t) \;=\; P(t)\,\hat{\varrho}(t) = \varrho_{rel}(t)\,,$$

respectively

$$P(t)\,\dot{\varrho}(t) \;=\; P(t)\,\dot{\hat{\varrho}}(t) = \dot{\varrho}_{rel}(t)\,.$$

Fick-Sauermann dynamics

The case (6) in which P maps $\varrho(t)$ specially to $R_{rel}(t)$ (cf. [8] [9]) has been treated by FICK and SAUERMANN [10]. Starting out with the VON NEUMANN equation (4) they derived the *Fick-Sauermann dynamics*

$$\begin{aligned} \dot{R}_{rel}(t) &= -i\big(P(t)\,L(t) + i\,\dot{P}(t)\big)\,R_{rel}(t) \\ &- \int_{t_0}^{t}\big(P(t)\,L(t) + i\,\dot{P}(t)\big)\,T(t,s)\,\big(Q(s)\,L(s) \\ &- i\,\dot{P}(s)\big)\,R_{rel}(s)\,ds \end{aligned} \tag{8}$$

with

$$\begin{aligned} \frac{\partial}{\partial s}\,T(t,s) &= i\,T(t,s)\,\big(Q(s)\,L(s) - i\,\dot{P}(s)\big)\,, \\ T(t,t) &= 1\,, \end{aligned}$$

and

$$\varrho(t_0) = R_{rel}(t_0)\,.$$

One possible operator P for this dynamics is the *Kawasaki-Gunton operator* [12]

$$P^{KG} : \mathcal{L} \to \mathcal{L}$$

$$P^{KG} X := R_{rel} \,\mathrm{tr} X + \frac{\partial R_{rel}}{\partial \mathbf{g}} \cdot (\mathrm{tr}\,(\mathbf{G}\, X) - \mathbf{g}\, \mathrm{tr} X)\ . \tag{9}$$

In this case, the dynamics (8) is an implicit differential equation, because $\dot{R}_{rel}$ is included in $\dot{P}^{KG}(t)$, which appears on the right hand side of the equation.

Robertson dynamics

Let us consider the dynamics using the local linear mapping (7). This case has been treated by ROBERTSON [13]. He started out with the VON NEUMANN equation (4) and assumed that $\varrho_{rel}(t)$ preserves the form of the generalized canonical operator for all time:

$$\dot{R}_{rel}(t) = P(t)\, \dot{\varrho}(t)\ . \tag{10}$$

Then he derived the so-called *Robertson dynamics*

$$\dot{R}_{rel}(t) = -i\, P(t)\, L(t)\, R_{rel}(t) - \int_{t_0}^{t} P(t)\, L(t)\, T(t,s)\, Q(s)\, L(s)\, R_{rel}(s)\, ds \tag{11}$$

with

$$\begin{aligned} \frac{\partial}{\partial s} T(t,s) &= i\, T(t,s)\, Q(s)\, L(s)\ , && (12)\\ T(t,t) &= 1\ , && (13)\\ \varrho(t_0) &= R_{rel}(t_0)\ . && (14) \end{aligned}$$

Although ROBERTSON derived this dynamics only for constant work variables, the dynamics remains its form also for time dependent work variables. However, we must now use an another mapping $P(t)$ than the ROBERTSON operator [13] or the KAWASAKI-GUNTON operator (9), which are used in ROBERTSON dynamics, because they only satisfy (10) if the work variables are constant in time. This problem is treated in [14] and partly in [15], too.

3. Positivity of entropy production

From (1) and (2) we get for the rate of entropy in canonical dynamics [2]:

$$\dot{S} = -k\, \mathrm{tr}\,(\dot{R}\, \ln R) = k\, \mathrm{tr}\,(\lambda \cdot \mathbf{G}\, \dot{R})\ . \tag{15}$$

The rate of entropy in an isolated system is called *entropy production* σ:

$$\sigma := \dot{S}\,\Big|_{\dot{\mathbf{a}}=\mathbf{0},\ \dot{Q}=0,\ \dot{\mathbf{n}}=\mathbf{0}}\ . \tag{16}$$

Considering a system $\mathcal{S}$ in contact with its environment $\mathcal{E}$ during a contact time Δt, that is sufficiently short, conduction problems are out of scope and exclusively the contact problem can be treated. If all the quantum mechanical drift terms [5] are vanishing in the chosen beobachtungsebene

$$\mathbf{v} := -i\, \mathrm{tr}\,(\mathbf{G} L R) = \mathbf{0}$$

and if we make a short time approximation (Taylor-expansion and neglecting quadratic and higher powers of Δt), the FICK-SAUERMANN dynamics using the KAWASAKI-GUNTON operator transforms into *contact time dynamics* [15]

$$\dot{R}_{rel} = P^{KG} R_{rel} - (P^{KG} L + i\,\dot{P}^{KG})(L - i\,\dot{P}^{KG})\, R_{rel}\, \Delta t\,.$$

The corresponding rate of entropy $\dot{S}$ and the entropy production σ of $\mathcal{S}$ can be calculated by inserting (8) into (15) and (16):

$$\sigma = \dot{S}\Big|_{\dot{\mathbf{a}}=\mathbf{0},\ \dot{Q}=0,\ \dot{\mathbf{n}}=\mathbf{0}} = k\,(i\,\lambda\cdot L\,\mathbf{G}\,\big|\,i\,\lambda\cdot L\,\mathbf{G})\,\Delta t \geq 0\,.$$

Here, the parentheses stand for the generalized MORI product [16]

$$(F\,\big|\,G) := \int_0^1 \operatorname{tr}(R_{rel}\,F^{+}\,R_{rel}^{u}\,G\,R_{rel}^{-u})\,du$$

which is a scalar product.

So it is possible to show the positivity of entropy production using this formalism.

4. Outlook

The question we are investigating is, if the maximum entropy principle is valid for systems in non-equilibrium, too. At this point, we can say that there are good prospects to answer this question in the near future using the formalism of quantum thermodynamics presented here.

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