Derivation of a two-generator framework of nonequilibrium thermodynamics for quantum systems

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Starting from the quantum description of isolated systems on the microscopic level we derive the two-generator formulation of nonequilibrium thermodynamics by means of the projection-operator technique. As a generalized canonical ensemble is employed, we obtain a convenient starting point for practical calculations in nonequilibrium thermodynamics; in particular, also in the classical limit. All dynamical material properties are contained in a canonical nonequilibrium correlation. However, the generalized canonical approach is inappropriate for systems with large fluctuations; possible steps toward a suitable generalization for quantum systems are discussed.

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I. INTRODUCTION

The understanding of nonequilibrium thermodynamics beyond the regime of linear constitutive equations is of great importance in many branches of science and engineering. In order to provide both a practical and general framework, a two-generator formulation of the time-evolution equations for nonequilibrium sytems, referred to as GENERIC (general equation for the nonequilibrium reversible-irreversible coupling), was deduced by considering the compatibility of two levels of description and by studying a large number of specific examples [1]. The key idea of the GENERIC framework is the use of two separate generators, energy and entropy, for the reversible and irreversible dynamics (this idea had previously been proposed in the context of plasma physics [2]). This is of crucial importance when treating systems without local equilibrium states, such as systems described by Boltzmann's kinetic equation.

The relationship between GENERIC and a number of alternative approaches to nonequilibrium thermodynamics has been established (see the summary in [3] and references therein). Moreover, a number of new results has been produced by this formulation of nonequilibrium thermodynamics. We here mention only the new insights into reptation models for melts of linear polymers [4], a modification of the Doi-Ohta model for multiphase flow [5], and new ways of producing equations for discrete hydrodynamics [6]. Moreover, the applicability of GENERIC to relativistic systems has been established. Covariant hydrodynamic equations of the GENERIC form have been proposed [7], a generally covariant version of the formalism has even been developed [8], and the implications for cosmological models have been explored [9].

Starting from Hamilton's equations of classical mechanics, the GENERIC form of coarse-grained time-evolution equations for the slow dynamic variables was derived by the standard projection-operator technique [10] (we here use the book [11] as a basic reference for the projection-operator technique). It is the goal of this work to derive GENERIC from a quantum mechanical description of an isolated microscopic system. While the generalized microcanonical derivation from classical mechanics [10] includes a description of large fluctuations in terms of stochastic differential equations with multiplicative noise, the present derivation for quantum systems is limited to situations with *negligible fluctuation effects*. In the final remarks, we comment on the possibility of including fluctuations and on the expected form of the corresponding fluctuation-dissipation theorem.

II. PROJECTION-OPERATOR APPROACH

In the projection-operator approach, one can account for the effects of the eliminated variables either by memory effects, while considering linear equations for the relevant variables, or by suitable nonlinearities, while using a Markovian approximation, or by a combination of both [11]. In order to arrive at GENERIC, one needs to keep sufficiently many variables and the appropriate nonlinearities for achieving a realistic description of a system by Markovian time-evolution equations.

We here consider the following situation. The relevant variables of an isolated nonequilibrium system with Hamilton operator H are given by the self-adjoint Hilbert space operators A_k, where k is a discrete or continuous label. Our goal is to determine time-evolution equations for the expectation values x_k of these generally noncommuting observables A_k by means of the projection-operator technique.

There are several fundamental differences between our approach and previous work on the projection-operator approach (as elegantly presented in Ref. [11]). First, we express the projected time-evolution equations in terms of two separate generators for reversible and irreversible contributions, whereas previously only one generator was used (either the free energy or the entropy [11]). Second, we do not treat the Hamiltonian separately in constructing projectors, nor do we insist on including it in the list of relevant variables, thus avoiding the concept of a global temperature constant typically occurring in one-generator theories and possible redundancies among the relevant variables. A further difference concerns the time evolution assumed in correlation functions occurring in Green-Kubo-type formulas.

A. Relevant density matrix

A key step in the projection-operator formalism is the identification of the relevant density matrix $\bar{\rho}$ when the fea-

tures of interest in a given system can be fully described in terms of the time-dependent variables $x=(x_k)$. We here assume that $\overline{\rho}=\overline{\rho}(x)$ has the following properties:

$$\mathrm{tr}\{\overline{\rho}(x)\}=1, \tag{1}$$

$$\mathrm{tr}\{\overline{\rho}(x)A_k\}=x_k, \tag{2}$$

and $\overline{\rho}(x)$ maximizes the entropy

$$S[\overline{\rho}]=-k_B\mathrm{tr}\{\overline{\rho}\ln\overline{\rho}\}, \tag{3}$$

where k_B is Boltzmann's constant. We obtain the following explicit expression for the density matrix of a generalized canonical form:

$$\overline{\rho}(x)=Z(x)^{-1}\exp\left(-\sum_k \lambda_k(x)A_k\right), \tag{4}$$

$$Z(x)=\mathrm{tr}\left\{\exp\left(-\sum_k \lambda_k(x)A_k\right)\right\}, \tag{5}$$

where the Lagrange multipliers $\lambda_k=\lambda_k(x)$ are determined by Eq. (2). The term ''generalized canonical'' emphasizes the fact that the list of variables A_k is much more general than in a canonical ensemble, so that Eq. (4) corresponds to ''quasiequilibrium'' states characterized by the slow variables x_k. We define the entropy $S(x)$ by inserting the density matrix (4) into Eq. (3) for $S[\overline{\rho}]$, thus obtaining

$$S(x)=k_B\left(\ln Z(x)+\sum_k \lambda_k(x)x_k\right). \tag{6}$$

Equations (2), (5), and (6) then lead to

$$\frac{\partial S(x)}{\partial x_k}=k_B\lambda_k(x), \tag{7}$$

which offers a nice interpretation of the Lagrange multipliers λ_k as the conjugates of the state variables x_k (leading to force-flux pairs). Of course, the total energy of the system is given by

$$E(x)=\mathrm{tr}\{\overline{\rho}(x)H\}. \tag{8}$$

The proposed construction of the relevant density matrix does not take into account possible symmetries, which may restrict the functional form of the density matrix in certain variables. For example, Galileian invariance should imply restrictions on the possible occurrence of velocities. Hence, in general, one should identify not only the relevant variables, but also the underlying symmetries. Work on the proper inclusion of symmetries in the construction of the relevant density matrix is in progress.

B. Projection operator

Following [11], we can now define the fundamental projection operator in terms of the relevant density matrix through the following action on arbitrary observables F:

$$P(x)F=\mathrm{tr}\{\overline{\rho}(x)F\}+\sum_k [A_k-x_k]\,\mathrm{tr}\left\{\frac{\partial\overline{\rho}(x)}{\partial x_k}F\right\}, \tag{9}$$

as well as the complementary projector $Q(x)=1-P(x)$. We also use the notation $P(t)=P(x(t))$, $Q(t)=Q(x(t))$. The projection-operator formalism can be based on the following rigorous identity, to be verified by differentiation with respect to time [11]:

$$e^{iLt}=e^{iLt}P(t)+Q(0)G(0,t)+\int_0^t e^{iLu}P(u)[iL-\dot{P}(u)]Q(u)G(u,t)du, \tag{10}$$

where the generator of time translations, L, in the Heisenberg picture operates on observables F as the commutator with the Hamilton operator divided by Planck's constant, $LF=[H,F]/\hbar$; the overdot indicates differentiation with respect to time; and in the time-ordered exponential

$$G(u,t)=T\exp\left(\int_u^t iLQ(s)ds\right) \tag{11}$$

the operators are ordered from left to right as time increases. The physical relevance of the formal identity (10) can be understood as follows: It expresses the well-known solution of the inhomogeneous linear differential equations for the slow observables, as projected out by $P(t)$, in the presence of inhomogeneities given by the rapid contributions, as projected out by $Q(t)$.

C. Exact time-evolution equation

By acting with both sides of Eq. (10) on iLA_j and averaging with respect to the initial density matrix $\overline{\rho}(x(0))$ we obtain an exact time-evolution equation for $x(t)$,

$$\frac{dx_j(t)}{dt}=\mathrm{tr}\{\overline{\rho}(x(t))iLA_j\}+\int_0^t \mathrm{tr}\{\overline{\rho}(x(u))iLQ(u)G(u,t)iLA_j\}du. \tag{12}$$

In deriving Eq. (12) we assumed that the exact initial density matrix is of the relevant form (4). This should be looked upon as a condition for the adequate definition of the relevant density matrix rather than a restriction of initial states [11].

In the following, the first term on the right-hand side of Eq. (12) is referred to as reversible and the second term as irreversible. The reversible term can be written as

$$\left[\frac{dx_j(t)}{dt}\right]_{\mathrm{rev}}=\frac{i}{\hbar}\mathrm{tr}\{\overline{\rho}(x(t))[H,A_j]\}. \tag{13}$$

The energy, as a conserved quantity, should certainly be among the slow variables. However, contrary to previous work, we here do not necessarily include H explicitly in the list of relevant observables, because this list typically contains internal energy and momentum densities, in terms of which the total energy can be expressed, and such redundancies need to be avoided. The *accessibility of the energy* through the relevant variables is hence expressed through the formal assumption

$$P(t)H=H. \tag{14}$$

With this assumption one obtains the final expression for the reversible contribution to the time evolution,

$$\left[\frac{dx_j(t)}{dt}\right]_{\rm rev}=\sum_k L_{jk}(x(t))\frac{\partial E(x(t))}{\partial x_k} \tag{15}$$

with the Poisson matrix

$$L_{jk}(x)=\frac{1}{i\hbar}\,{\rm tr}\{\overline{\rho}(x)[A_j,A_k]\}. \tag{16}$$

By means of the operator identity

$$[e^{-A},B]=e^{-A}\int_0^1 e^{\xi A}[B,A]e^{-\xi A}d\xi, \tag{17}$$

we obtain the following still exact result for the irreversible contribution in Eq. (12):

$$\begin{aligned}\left[\frac{dx_j(t)}{dt}\right]_{\rm irr}&=\left(\frac{i}{\hbar}\right)^2\int_0^t {\rm tr}\{[\overline{\rho}(x(u)),H]Q(u)G(u,t)[H,A_j]\}du\\&=\left(\frac{i}{\hbar}\right)^2\int_0^t \lambda_k(x(u))\,{\rm tr}\{\overline{\rho}(x(u))[H,A_k]^{(s)}_{x(u)}Q(u)\\&\quad\times G(u,t)[H,A_j]\}du\end{aligned} \tag{18}$$

with

$$[H,A_k]^{(s)}_x=\int_0^1 e^{\xi\sum_l \lambda_l(x)A_l}[H,A_k]e^{-\xi\sum_l \lambda_l(x)A_l}d\xi. \tag{19}$$

D. Markovian approximation

The crucial assumption of the projection-operator formalism now is that there should exist a clear separation of time scales. The relevant variables x_k evolve on a time scale large compared to some intermediate scale τ, and all other variables evolve rapidly compared to τ. Experience shows that this situation exists for many macroscopic systems of interest [11]. In view of the occurrence of the projectors Q (projecting on the fast variables) in the integral of Eq. (18), the integrand should decay rapidly, and the integral is expected to be dominated by values of u between $t-\tau$ and t. Then, all slow variables in the integral can be evaluated at time t and, in particular, $\lambda_k(x(u))$ can be pulled out of the integral as $\lambda_k(x(t))$. With Eq. (7) we then obtain the following approximate version of Eq. (18):

$$\left[\frac{dx_j(t)}{dt}\right]_{\rm irr}=\sum_k M_{jk}(x(t))\frac{\partial S(x(t))}{\partial x_k} \tag{20}$$

with the friction matrix

$$\begin{aligned}M_{jk}(x)=\frac{1}{k_B}\left(\frac{i}{\hbar}\right)^2\int_0^\tau {\rm tr}\{\overline{\rho}(x)[H,A_k]^{(s)}_x Q(x)e^{iLQ(x)u}Q(x)\\\times[H,A_j]\}du.\end{aligned} \tag{21}$$

It is customary to neglect the projector $Q(x)$ occurring in the exponential of this expression, which then leads to

$$\begin{aligned}M_{jk}(x)=\frac{1}{k_B}\left(\frac{i}{\hbar}\right)^2\int_0^\tau {\rm tr}\{\overline{\rho}(x)[H,A_k]^{(s)}_x Q(x)e^{iHu/\hbar}Q(x)\\\times[H,A_j]e^{-iHu/\hbar}\}du.\end{aligned} \tag{22}$$

However, this last approximation is not necessary in order to obtain the decomposition (20). From a practical point of view, it might even be advantageous to keep the projector Q because, in a computer simulation, it would allow us to bring in information about the underlying nonequilibrium state x, for which the friction matrix is to be evaluated, after every time step.

Equations (21) and (22) can be expressed conveniently in terms of the *canonical nonequilibrium correlation*

$$\langle A;B\rangle_x=\int_0^1 {\rm tr}\left\{\overline{\rho}(x)e^{\xi\sum_k \lambda_k(x)A_k}Ae^{-\xi\sum_k \lambda_k(x)A_k}B\right\}d\xi, \tag{23}$$

which is the natural generalization of the analogous canonical correlation of Kubo *et al.* [12] (the original canonical correlation is based on a density matrix proportional to $\exp[-H/(k_BT)]$), and closely related to Grabert's generalized canonical correlation [11] (as mentioned before, we here avoid the prominent role of H in the list of relevant variables). This generalization is necessary for going from near-equilibrium to far-from-equilibrium situations. The twofold role of the Hamiltonian in the time evolution and in the density matrix, which leads to considerable mathematical simplifications near equilibrium (see, e.g., temperature Green's functions [12]), is lost in moving far away from equilibrium.

E. GENERIC properties

In summary, we have derived the time-evolution equation

$$\frac{dx_j}{dt}=\sum_k\left(L_{jk}(x)\frac{\partial E(x)}{\partial x_k}+M_{jk}(x)\frac{\partial S(x)}{\partial x_k}\right), \tag{24}$$

where the building blocks S, E, L, and M are given by the microscopic expressions (6), (8), (16), and (21), respectively. In this equation, memory effects are eliminated in favor of nonlinearities in x. The time-evolution equation (24) holds far from equilibrium; the basic assumption is that the nonequilibrium states of the system of interest can be characterized by the observables A_k with expectations x_k.

Note that Eq. (24) is the fundamental equation of the GENERIC framework. Various properties of the building blocks can immediately be derived from the microscopic expressions, such as the antisymmetry of the matrix L_{jk} from Eq. (16). The fact that $\overline{\rho}(x)$ commutes with $\Sigma_k \lambda_k(x)A_k$ implies the degeneracy requirement

$$\sum_k L_{jk}(x)\frac{\partial S(x)}{\partial x_k}=0, \tag{25}$$

which is an important part of the GENERIC framework [1]. The other basic degeneracy requirement of that framework,

$$\sum_k M_{jk}(x)\frac{\partial E(x)}{\partial x_k}=0, \tag{26}$$

can be shown only when the possibly approximate assumption (14) expressing the accessibility of energy may be used [the situation concerning the rigor of proofing the mutual degeneracy requirements (25) and (26) is hence reversed compared to the previous work [10], where a generalized microcanonical description of a classical system was employed]. Other properties, such as the Jacobi identity expressing the time-structure invariance of the Poisson bracket associated with the antisymmetric matrix L [1], remain to be shown (cf. comments in [3]).

III. CONCLUDING REMARKS

The fact that the building blocks (6), (8), (16), and (21) of GENERIC arise so naturally from the projection-operator formalism applied to isolated quantum systems provides a further argument in favor of the two-generator approach to nonequilibrium thermodynamics. Without any modifications, the GENERIC framework is now established to be consistent not only with special [7] and general [8] relativity, but also with quantum mechanics.

The integrand occurring in Eq. (21) should be considered as the most natural nonequilibrium correlation function for quantum systems. The results of this work are of great help also for classical systems because they indicate how to move from a generalized microcanonical ensemble [10] to a generalized canonical nonequilibrium ensemble. As in equilibrium thermodynamics, this should be helpful in practical calculations and, in particular, the classical counterparts of the formulas derived in this work might be used as a starting point for nonequilibrium Monte Carlo and molecular dynamics simulations.

Compared to the previous result for the generalized microcanonical ensemble for a classical system [10], the expressions (16) and (21) for the Poisson and friction matrices obtained after replacing commutators by Poisson brackets are formally identical, which is a remarkable result. The only difference is that $\overline{\rho}$ here represents the generalized canonical ensemble (4) instead of a microcanonical ensemble. This difference does not matter as long as fluctuations are negligibly small. By arguments analogous to those used in equilibrium statistical mechanics (see, e.g., Sec. 2.4 of [13]), we expect sharply peaked contributions to averages for both the microcanonical and the canonical ensembles. However, when fluctuations become large, the assumption of a generalized canonical ensemble (4) in terms of the averages of the relevant observables becomes inappropriate. The more detailed classical projection-operator result for distribution functions as relevant variables shows that the GENERIC (24) should be replaced by the Itô stochastic differential equations

$$\frac{dx_j}{dt}=\sum_k\left(L_{jk}(x)\frac{\partial E(x)}{\partial x_k}+M_{jk}(x)\frac{\partial S(x)}{\partial x_k}+k_B\frac{\partial M_{jk}(x)}{\partial x_k}\right)+\sum_\nu B_{j\nu}(x)\frac{dW_\nu}{dt}, \tag{27}$$

where the W_ν are independent Wiener processes [14], and their configuration-dependent prefactors $B_{j\nu}$ are given by the *fluctuation-dissipation theorem* of the second kind [12],

$$\sum_\nu B_{j\nu}(x)B_{k\nu}(x)=2k_BM_{jk}(x). \tag{28}$$

The configuration-dependent or multiplicative and hence non-Gaussian noise in Eq. (27) implies nontrivial fluctuation effects on the averages of the stochastic processes x_k, which are known as fluctuation renormalization [11].

For quantum systems also, it would be convenient to describe thermal fluctuations by stochastic differential equations for the expectations of the operators A_k, rather than by time-evolution equations for some density matrix [11], because one would like to have a self-contained description on the coarse-grained level, and because efficient integration schemes are known for stochastic differential equations [14]. It is natural to assume that even in the quantum case we recover the equations (27) and (28) for the thermal noise. As in equilibrium thermodynamics, the structure of the coarse-grained equations should not depend on the classical or quantum nature of the microscopic system, whereas the explicit expressions for the building blocks (a thermodynamic potential for an equilibrium system; E, S, L, M for a nonequilibrium system) should occur as natural generalizations in going from classical to quantum systems. Moreover, canonical correlations naturally occur in the fluctuation-dissipation theorem [12]. While the generalized canonical ensemble clearly becomes inappropriate for evaluating the Poisson and friction matrices (16) and (21) in the presence of large fluctuations, it is not obvious what density matrix should then be used in these expressions. A generalized microcanonical ensemble with sharp values for the observables A_k does not exist in a quantum mechanical system because, in general, the observables A_k do not commute. The proper coupling of the quantum fluctuations resulting from Heisenberg's uncertainty principle and of the thermal fluctuations resulting from coarse graining should be achieved by constructing a quantum microcanonical nonequilibrium ensemble with uniformly as well-defined values of the observables A_k as allowed by their commutation relations. Wigner distribution functions as relevant variables [13,15,16] would provide a convenient mathematical tool for developing the corresponding projection-operator formalism.

[1] M. Grmela and H.C. Öttinger, Phys. Rev. E **56**, 6620 (1997); H.C. Öttinger and M. Grmela, *ibid.* **56**, 6633 (1997).

[2] A.N. Kaufman, Phys. Lett. **100A**, 419 (1984).

[3] J.J. de Pablo and H.C. Öttinger, J. Non-Newtonian Fluid Mech. (to be published).

[4] H.C. Öttinger and A.N. Beris, J. Chem. Phys. **110**, 6593 (1999); H.C. Öttinger, J. Non-Newtonian Fluid Mech. **89**, 165 (1999); H.C. Öttinger, J. Rheol. **43**, 1461 (1999).

[5] N.J. Wagner, H.C. Öttinger, and B.J. Edwards, AIChE J. **45**, 1169 (1999).

[6] P. Español, M. Serrano, and H.C. Öttinger, Phys. Rev. Lett. **83**, 4542 (1999).

[7] H.C. Öttinger, Physica A **259**, 24 (1998); **254**, 433 (1998).

[8] H.C. Öttinger, Phys. Rev. D **60**, 103507 (1999).

[9] P. Ilg and H.C. Öttinger, Phys. Rev. D **61**, 023510 (2000).
[10] H.C. Öttinger, Phys. Rev. E **57**, 1416 (1998).
[11] H. Grabert, *Projection Operator Techniques in Nonequilibrium Statistical Mechanics* (Springer, Berlin, 1982).
[12] R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II, Nonequilibrium Statistical Mechanics*, 2nd ed. (Springer, Berlin, 1991).
[13] M. Toda, R. Kubo, and N. Saitô, *Statistical Physics I, Equilibrium Statistical Mechanics*, 2nd ed. (Springer, Berlin, 1992).
[14] H.C. Öttinger, *Stochastic Processes in Polymeric Fluids. Tools and Examples for Developing Simulation Algorithms* (Springer, Berlin, 1996).
[15] H. Mori, I. Oppenheim, and J. Ross, in *Studies in Statistical Mechanics*, Vol. 1, edited by J. de Boer and G.E. Uhlenbeck (North-Holland, Amsterdam, 1962).
[16] M. Hillery, R.F. O'Connell, M.O. Scully, and E.P. Wigner, Phys. Rep. **106**, 121 (1984).