PHYSICAL REVIEW E **90**, 062131 (2014)

Time reversal in nonequilibrium thermodynamics

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(Received 11 September 2014; published 19 December 2014)

The general equation of nonequilibrium reversible-irreversible coupling (GENERIC) is studied in light of time-reversal transformation. It is shown that Onsager-Casimir reciprocal relations are implied by GENERIC in the near-equilibrium regime. A general structure which gives the reciprocal relations but which is valid also far from equilibrium is identified, and Onsager-Casimir reciprocal relations are generalized to far-from-equilibrium regime in this sense. Moreover, reversibility and irreversibility are carefully discussed and the results are illustrated in Hamiltonian dynamics, classical hydrodynamics, classical irreversible thermodynamics, the quantum master equation, and the Boltzmann equation.

DOI: 10.1103/PhysRevE.90.062131 PACS number(s): 05.70.Ln, 05.90.+m

I. INTRODUCTION

The mesoscopic time evolution of macroscopic systems is experimentally observed to be time irreversible and dissipative. The former property means, roughly speaking, that the trajectories that begin at the moment at which the time has been reversed are not seen to be retracing the trajectories followed in the previous evolution. The latter property then means that there exists a potential, called entropy, that does not decrease during the time evolution. Our objective in this paper is to define carefully both the irreversibility and the dissipativity and to investigate their relationship and consequences. Such an investigation can also be seen as an investigation of the Onsager-Casimir reciprocal relations (OCRR) [1–3] in the context of far-from-equilibrium nonlinear mesoscopic dynamics possessing the structure of general equation of nonequilibrium reversible and irreversible coupling (GENERIC). In particular, it is shown that the Hamiltonian part of the time evolution is responsible for the antisymmetric coupling (discovered originally by Casimir [3]) while the dissipation potential is responsible for the symmetric coupling. GENERIC enriched with some assumptions on its behavior with respect to time-reversal transformation (TRT) is then the far-from-equilibrium structure which yields OCRR near equilibrium.

Finally, the results are illustrated in Hamiltonian dynamics, classical hydrodynamics, the theory of mixtures within classical irreversible thermodynamics (CIT), the finite-dimensional quantum master equation, and the Boltzmann equation.

II. STRUCTURE OF NONEQUILIBRIUM THERMODYNAMICS

A. Time-reversal transformation

Let us first recall the notion of time-reversal transformation [1,4]. Imagine a movie depicting motion of particles in an isolated box. Suppose that the particles behave classically, i.e., their motion is described by Newton's law,

$$\dot{\mathbf{p}}_i = \mathbf{F_i}, \tag{2.1}$$

where $\mathbf{p}_i$ is momentum of the i-th particle and $\mathbf{F}_i$ is force exerted on the i-th particle by other particles and walls of the box. If the movie is played backwards, one can see that velocities of the particles are reversed [5] and that the time stamp goes in the opposite direction. This thought experiment constitutes physical motivation for introducing TRT, which is to be denoted by $\mathbf{I}$.

Definition 1 [(TRT)]. TRT transforms any physical quantity exactly in the same way as if velocities of all particles were reversed. Moreover, the time stamp goes in the opposite direction.

Let us now study properties of the transformation. Consider a state variable x_i, where i can be a discrete or a continuous index. If velocities of all particles were reversed, the state variable x_i would change to $\mathbf{I}(x_i)$. If, however, the velocities were reversed once more, the variable must return to the original value, i.e.,

$$\mathbf{I}(\mathbf{I}(x_i)) = x_i. \tag{2.2}$$

Hence, operation $\mathbf{I}$ is idempotent.

If TRT does not alter the state variable or if it only changes sign of the variable, we say that the variable has even or odd parity, respectively. Parity of state variable x_i is denoted by $\mathcal{P}(x_i)$ and we say that

$$\mathcal{P}(x_i) = 1 \quad \text{for} \quad x_i \text{ even}, \tag{2.3}$$

$$\mathcal{P}(x_i) = -1 \quad \text{for} \quad x_i \text{ odd}. \tag{2.4}$$

For example, momenta of particles in the box are odd as $\mathbf{I}(\mathbf{p}_i) = -\mathbf{p}_i$. On the other hand, positions of the particles are even. It should be noted that not all state variables have parity. For example, if we choose the probability density of position and momentum (as in Boltzmann equation) as a state variable, we obtain

$$\mathbf{I}(f(\mathbf{r},\mathbf{v})) = f(\mathbf{r}, -\mathbf{v}) \tag{2.5}$$

and this state variable has clearly no parity. In summary, parity then can be defined as follows:

Definition 2 (Parity). A physical quantity has parity equal to 1 if TRT does not alter the quantity, i.e., the quantity is even under TRT. A physical quantity has parity equal to −1 if TRT

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inverts the sign of the quantity, i.e., the quantity is odd under TRT.

TRT can be also applied to the time derivative of a state variable. Since the time stamp of the inverted movie goes backwards, TRT acts on the time derivative as follows:

$$\mathbf{I}\left(\frac{dx_i}{dt}\right) = -\frac{d}{d\tau}\mathbf{I}(x_i), \tag{2.6}$$

where the backward-going time step was denoted by $d\tau$. Note that if the state variable is a field variable, for example, momentum density $\mathbf{u}(\mathbf{r},t)$, the time derivative in the preceding formula stands for the partial time derivative.

So far we have talked about TRT acting on state variables. Let us now have a look at how TRT transforms evolution equations. Consider, for example, the incompressible Navier-Stokes equation [6],

$$\frac{\partial\rho}{\partial t} = -\frac{\mathbf{u}}{\rho}\cdot\nabla\rho, \tag{2.7}$$

$$\frac{\partial\mathbf{u}}{\partial t} = -\mathrm{div}\left(\frac{1}{\rho}\mathbf{u}\otimes\mathbf{u}\right) - \nabla p + \mu\Delta\left(\frac{\mathbf{u}}{\rho}\right), \tag{2.8}$$

where ρ is the density field and $\mathbf{u}$ is the momentum density field. The former equation expresses evolution of density while the latter evolution of momentum density. Application of TRT then gives

$$-\frac{\partial\rho}{\partial\tau} = +\frac{\mathbf{u}}{\rho}\cdot\nabla\rho, \tag{2.9}$$

$$\frac{\partial\mathbf{u}}{\partial\tau} = -\mathrm{div}\left(\frac{1}{\rho}\mathbf{u}\otimes\mathbf{u}\right) - \nabla p - \mu\Delta\left(\frac{\mathbf{u}}{\rho}\right). \tag{2.10}$$

Here we used that density and pressure are even variables while momentum density is odd under TRT. Obviously, evolution equation for density is not altered by TRT. On the other hand, the sign of the viscous part of the evolution equation of momentum density is changed. This means that if there were no viscosity, evolution equations (2.7) and (2.8) would describe motion of the fluid even if the movie were played backwards. With nonzero viscosity, this is not true anymore.

Based on this motivation, let us now define reversible and irreversible part of an evolution equation.

Definition 3 (reversibility based on TRT). Assume that the evolution equation is solved with respect to time derivative, i.e., is in the form where, on the left-hand side, there is only the time derivative of the state variable evolution, which the equation describes. Moreover, assume that there are no time derivatives on the rigt-hand side of the equation. The reversible part of the evolution equation is then defined as the part of the right-hand side which is transformed by TRT in the same way as the left-hand side of the equation. The irreversible part is then the rest of the right-hand side of the evolution equation.

For example, the right-hand side of Eq. (2.7) transforms in the same way as the left-hand side of the equation. Indeed, Eq. (2.9) has the same form as Eq. (2.7). The gradient of pressure on the right-hand side of Eq. (2.8) is even as is the left-hand side of the equation. On the other hand, the viscous part is odd. Therefore, gradient of pressure generates reversible evolution while the viscous part is irreversible. The case where state variables have no parity will be commented on later when analyzing the Boltzmann equation. This definition of reversibility can be expressed more rigorously within differential geometrically, see Sec. II E.

B. Structure of GENERIC

Within the GENERIC [7–9] framework each evolution equation is expressed in the following form:

$$\frac{dx_i}{dt} = \sum_j L_{ij}E_{x_j} + \frac{\delta\Xi}{\delta S_{x_i}}, \tag{2.11}$$

where L_{ij} represents the Poisson bivector field, Ξ is the dissipation potential, E is energy, and S is the entropy of the system under consideration. The Poisson bracket between any two functionals A and B may be constructed from the Poisson bivector as

$$\{A,B\} = \langle A,\mathbf{L}B\rangle, \tag{2.12}$$

where $\langle\bullet,\bullet\rangle$ represents the scalar product in an appropriate space of state variables [9]. The Poisson bracket is antisymmetric and fulfills the Jacobi identity. The dissipation potential is supposed to be a convex function of thermodynamic force S_{x_i} near $S_{x_i}=0$; it is zero for the force equal to zero and it reaches the minimum for $S_{x_i}=0$ (see Ref. [9] for more details).

Moreover, approximating the dissipation potential by a quadratic function in forces (here denoted by $\mathbf{X}$), i.e., exploiting convexity of the dissipation potential near equilibrium,

$$\Xi = \tfrac{1}{2}\langle\mathbf{X},\mathbf{M}\mathbf{X}\rangle \tag{2.13}$$

leads to formulation of a dissipative bracket,

$$[A,B] = \langle A_{\mathbf{x}},\mathbf{M}\cdot B_{\mathbf{x}}\rangle. \tag{2.14}$$

In this way evolution equation (2.11) may be approximated by the following evolution equation:

$$\frac{dx_i}{dt} = \sum_j L_{ij}E_{x_j} + \sum_j M_{ij}S_{x_j}, \tag{2.15}$$

where M_{ij} is the dissipative matrix, which is symmetric and positive definite. Moreover, both matrices are assumed to fulfill the following degeneracy conditions:

$$\sum_j L_{ij}S_{x_j} = 0 = \sum_j M_{ij}E_{x_j}, \tag{2.16}$$

which guarantees the separation of the antisymmetric (reversible, see Theorem 1 below) and symmetric (irreversible, see Theorem 1 below) parts of a given evolution equation.

Note that if i and j are continuous indices, e.g., position vectors $\mathbf{r}$ and $\mathbf{r}'$, respectively, matrix multiplication in (2.15) also consists of integration with respect to $\mathbf{r}'$. We also suppose that the system, which is to be described, is isolated, infinite, or periodic, so boundary terms disappear when integrating by parts.

In the whole paper we use the following assumption:

Assumption 1. We assume that evolution equations of any physical system can be written in the GENERIC form. Therefore, we limit ourselves to such time evolution that, from the physical point of view, describes systems approaching a reduced description (e.g., to the description used in classical thermodynamics).

Evolution equation (2.15) can be equivalently expressed in terms of a thermodynamic potential,

$$\Phi(\mathbf{x}) = -S(\mathbf{x}) + \frac{1}{T^0}E(\mathbf{x}) - \frac{\mu^0}{T^0}N(\mathbf{x}), \tag{2.17}$$

where T^0 is the equilibrium temperature, μ^0 is the equilibrium chemical potential, and N is the amount of mass in the system. Note that neither the Poisson bracket nor the dissipative bracket (or dissipation potential) alter the amount of mass $N(\mathbf{x})$ [and also energy $E(\mathbf{x})$ as we have seen above]. Equation (2.15) then becomes

$$\frac{dx_i}{dt} = (T^0 L_{ij} - M_{ij})\Phi_{x_j}. \tag{2.18}$$

Both equations (2.15) and (2.18) are equivalent because of the degeneracies of the brackets.

It is important to emphasize that the properties of the operators L and M (or, more generally, the properties of L and the dissipation potential Ξ) that we required above imply that the thermodynamic potential Φ [given in (2.18)] plays the role of the Lyapunov function for the approach to states that are solutions to $\frac{\delta\Phi}{\delta x} = 0$ provided $\Phi(x)$ is a convex function of x. Indeed, we see immediately that $\frac{d\Phi}{dt} \leqslant 0$. From the physical point of view, a solution to $\frac{\delta\Phi}{\delta x} = 0$ is a thermodynamic equilibrium state [we denote it $x_{\text{th}}(\mu_0,T_0)$] and $-\frac{P_0}{V} = \Phi(x_{\text{th}}(\mu_0,T_0))$ is the equilibrium thermodynamics fundamental thermodynamic relation implied by the GENERIC time evolution governed by (2.11). The symbol P_0 stands for the equilibrium pressure and V for the volume of the region in $\mathbb{R}^3$ in which the macroscopic system under consideration is confined. We assume that the confinement is fixed so V is a constant.

We thus see that from the physical point of view, the GENERIC equation (2.11) represents a passage from the mesoscopic level on which x plays the role of state variables to the level of equilibrium thermodynamics on which (V,E,N), where $E = E(x_{\text{th}}), N = N(x_{\text{th}})$, or, alternatively, (T_0,μ_0) serve as state variables. It means that however far from equilibrium we may be, the time evolution is still influenced by the total energy and the total mass (since they remain constant during the time evolution) and, consequently, since $\frac{d\Phi}{dt} \leqslant 0$, by the equilibrium thermodynamic state approached as $t \to \infty$. This physical content of GENERIC (2.11) is manifestly displayed in the appearance of two parameters [T_0 and μ_0 in (2.18)]. Note that this is just an alternative formulation of two parameters, namely the total energy and the total mass, appearing (implicitly) in (2.11). A geometrical formulation of GENERIC (in terms of the contact structure geometry) that manifestly presents itself as a time evolution representing a passage between two levels (one of which is not necessarily the level of equilibrium thermodynamics) can also be discussed [9,10].

C. On equivalence of notions of reversibility

In the GENERIC framework the notion of reversibility is such that [7,8]

Definition 4 (reversibility within GENERIC). The Poisson bracket generates reversible evolution while the dissipation potential (or the dissipative bracket) generates irreversible evolution.

On the other hand, reversible processes in an isolated system are often identified [6] via entropic arguments:

Definition 5 (entropic reversibility). Reversible evolution of an isolated system does not raise entropy, i.e., $\dot{S} = 0$, while irreversible evolution raises entropy.

Are these two notions of reversibility and irreversibility compatible? Moreover, are they compatible with Definition 3 of reversibility based on TRT?

The evolution equation of a functional A can be formulated using Poisson and dissipative brackets as

$$\frac{dA}{dt} = \{A,E\} + [A,S], \tag{2.19}$$

which follows from equation (2.15) and the definitions of the Poisson bracket and dissipative bracket. In particular, consider A as the entropy, the evolution equation of which is the following [due to the degeneracy conditions (2.16)]:

$$\frac{dS}{dt} = \{S,E\} + [S,S] = [S,S] \geqslant 0, \tag{2.20}$$

and where

$$\frac{dS}{dt} = 0 \Longleftrightarrow [S,S] = 0. \tag{2.21}$$

Therefore, if the dissipative matrix or bracket is not present in the evolution equation of the state variable x_i, Eq. (2.15), the evolution equation describes some reversible processes within the system in the sense of Definition 5 regarding entropic reversibility. Thus, reversible processes in the sense of Definition 4 do not raise the entropy of an isolated system, and these two notions of reversibility and irreversibility are in agreement. The same conclusion holds if the dissipation potential is used instead of the dissipative bracket. Thus we have just proven the following lemma:

Lemma 1. Definition 4 of reversibility or irreversibility within GENERIC and the entropic Definition 5 are equivalent.

Are these two notions of reversibility compatible with Definition 3 of TRT-based reversibility or irreversibility?

Assume that all state variables have definite parities, which means that

$$\mathbf{I}(x_i) = \mathcal{P}(x_i)x_i = \pm x_i. \tag{2.22}$$

What is the parity of the functionals generating the evolution, E and S? In the whole paper we use the following assumption:

Assumption 2 (parity of E, S, Φ, and Ξ). Energy, entropy, thermodynamic potential, and dissipation potential are assumed to be even under TRT.

For energy the assumption is quite natural since if energy (or the Hamiltonian) were not even, Hamilton equations would not be reversible, see Sec. III A. For entropy, the assumption also seems to be quite natural since we are not aware, to the best of our knowledge, of any particular example of noneven entropy. For example, if entropy is constructed as $S = -k\sum_i p_i \ln p_i$ as is usual in statistical mechanics [11], the entropy is obviously even. Moreover, nonequilibrium statistical physics also leads to the same conclusion [4]. The statement that entropy is even should, however, be taken as an assumption. Thermodynamic potential is even since it is formed from energy and entropy, which are supposed to be even. The assumption that the dissipation potential is even is also natural (see Sec. II E), where it is shown that this property of dissipation potential is needed to make all the three definitions of irreversibility equivalent. This property of the dissipation potential is fulfilled for all dissipation potentials used in this manuscript, and we are not aware of any noneven dissipation potential describing real systems.

Application of TRT on Eq. (2.15) then yields

$$-\mathcal{P}(x_i)\frac{dx_i}{d\tau} = \sum_j \mathcal{P}(L_{ij})L_{ij}\mathcal{P}(x_j)E_{x_j} + \sum_j \mathcal{P}(M_{ij})M_{ij}\mathcal{P}(x_j)S_{x_j}, \tag{2.23}$$

since functionals E and S are assumed to be even. This last equation can be rewritten as

$$\frac{dx_i}{d\tau} = -\sum_j \mathcal{P}(L_{ij})\mathcal{P}(x_i)\mathcal{P}(x_j)L_{ij}E_{x_j} - \sum_j \mathcal{P}(M_{ij})\mathcal{P}(x_i)\mathcal{P}(x_j)M_{ij}S_{x_j}. \tag{2.24}$$

The first term on the right-hand side of Eq. (2.15) causes reversible evolution in the sense of Definition 4 while the second term causes irreversible evolution. For the two definitions 3 and 4 to be compatible, it is necessary that after application of TRT the first term does not alter structure of the equation while the second does. In other words, the first term on the right-hand side of Eq. (2.24) must be the same as the first term on the right-hand side of Eq. (2.15) while the second term must have opposite sign than the second term on the right-hand side of Eq. (2.15), i.e.,

$$\mathcal{P}(L_{ij}) = -\mathcal{P}(x_i)\mathcal{P}(x_j), \tag{2.25a}$$

$$\mathcal{P}(M_{ij}) = \mathcal{P}(x_i)\mathcal{P}(x_j). \tag{2.25b}$$

These two equations are the necessary and sufficient conditions for the notion of reversibility within GENERIC, Definition 4, to be equivalent to the definition of reversibility in the sense of Definition 3. This conclusion may be formulated as the following theorem:

Theorem 1 (equivalence of definitions of reversibility). Under these assumptions:

(1) All variables have definite parities.
(2) Assumption 2 holds true.
(3) Relations (2.25) are fulfilled.

The three definitions of reversibility-irreversibility (3, 4, and 5) are equivalent.

Note that the second relation (2.25b) can be seen as a consequence of the fact that the dissipation potential is even. Indeed, parity of the quadratic dissipation potential (2.13) can be written as

$$1 = \mathcal{P}(S_{x_i}M_{ij}S_{x_j}) = \mathcal{P}(x_i)\mathcal{P}(x_j)\mathcal{P}(M_{ij}), \tag{2.26}$$

which is equivalent to the second relation of (2.25).

In Sec. II E Definition 3 is formulated geometrically and Theorem 1 is generalized. Moreover, it is shown that Assumption 2 is sufficient to replace the second relation from (2.25) not only in the case of a dissipative bracket. In other words, the dissipation potential generates only irreversible evolution automatically, and the second relation in (2.25) is redundant if we work with the dissipation potential instead of dissipative bracket.

D. Onsager-Casimir reciprocal relations

In this section we show that OCRR are implied by GENERIC with conditions (2.25) near equilibrium. Near equilibrium the general evolution equation (2.18) becomes [7]

$$\dot{\xi}_i = \sum_j \sum_k [TL_{ij}(x_{\text{th}}) - M_{ij}(x_{\text{th}})]\frac{\delta^2\Phi}{\delta x_j \delta x_k}(x_{\text{th}})\xi_k, \tag{2.27}$$

where the thermodynamic potential is approximated by quadratic terms and both brackets are evaluated at equilibrium. ξ_i denotes deviation of variable x_i from the equilibrium value of the variable. This equation can be rewritten in the standard form of near-equilibrium evolution,

$$\dot{\xi}_i = \sum_j K_{ij}X_j, \tag{2.28}$$

where the matrix of phenomenological coefficients $\mathbf{K}$ is defined as

$$K_{ij} = TL_{ij}(x_{\text{th}}) - M_{ij}(x_{\text{th}}) \tag{2.29}$$

and the thermodynamic force $\mathbf{X}$ is defined as

$$X_j = \sum_k \frac{\delta^2\Phi}{\delta x_j \delta x_k}(x_{\text{th}})\xi_k. \tag{2.30}$$

The matrix $\mathbf{K}$ depends only on equilibrium values of state variables (hence not evolving with time). Usually, the equilibrium values are even under TRT because odd variables, e.g., momentum, vanish at equilibrium. Therefore, each element of the matrix is even as well,

$$\mathcal{P}(\mathbf{K}) = 1. \tag{2.31}$$

Analogously, the same is true for matrices $\mathbf{L}$ and $\mathbf{M}$ evaluated at equilibrium, i.e.,

$$\mathcal{P}(L_{ij}(x_{\text{th}})) = \mathcal{P}(M_{ij}(x_{\text{th}})) = 1. \tag{2.32}$$

Comparing to parities indicated in relations (2.25), it follows that all terms corresponding to state variables with $\mathcal{P}(x_i)\mathcal{P}(x_j) = 1$, i.e., with the same parities, vanish in $L_{ij}(x_{\text{th}})$ while all terms corresponding to state variables with $\mathcal{P}(x_i)\mathcal{P}(x_j) = -1$, i.e., with opposite parities, vanish in $M_{ij}(x_{\text{th}})$.

Therefore, we have derived that $L_{ij}(x_{\text{th}})$ is responsible for coupling between state variables of different parities only while $M_{ij}(x_{\text{th}})$ is responsible for coupling only between state variables with the same parities. Now, from the antisymmetry of $\mathbf{L}$ and symmetry of $\mathbf{M}$, we obtain Onsager-Casimir reciprocal relations, which say that state variables with the same parities are coupled through a symmetric matrix while state variables with opposite parities are coupled through an antisymmetric matrix. OCRR can be thus regarded as a consequence of GENERIC and the behavior of GENERIC with respect to TRT. Let us now formulate these conclusions as a theorem:

Theorem 2. Let us assume that

(1) Assumption 1 holds.

(2) Parity may be assigned to each state variable x_i, i.e., $\mathcal{P}(x_i)$ is well defined, $\forall x_i$.

(3) Both matrices L_{ij} and M_{ij} are even with respect to TRT if evaluated at equilibrium. This is true, for example, if the matrices are constructed from spatial gradients and state variables.

(4) Relations (2.25) are valid.

(5) Assumption 2 holds and thus definitions of reversibility 3, 4, and 5 are equivalent according to Theorem 1.

Then state variables with the opposite parities are coupled through the antisymmetric part of the matrix K_{ij} in Eq. (2.28) while state variables with the same parity are coupled through the symmetric part in the near-equilibrium regime. This is the statement of Onsager-Casimir reciprocal relations, which are thus proved for any system near equilibrium.

Corollary 1. Since the symmetric part is given by the dissipative bracket and the antisymmetric by the Poisson bracket, it follows that state variables with opposite parities are coupled only through the Poisson bracket while state variables with the same parities are coupled only through the dissipative bracket near equilibrium.

We have, therefore, shown that the structure of GENERIC and its behavior with respect to TRT implies OCRR near equilibrium. This means that we have identified the general structure which contains OCRR and which is valid far from equilibrium. In this sense, GENERIC intrinsically contains OCRR and thus can be considered as a generalization of OCRR into far from equilibrium regime. Note that other thermodynamic theories like classical irreversible thermodynamics (CIT) [6] or extended irreversible thermodynamics (EIT) [12] do not posses this property since OCRR have to be supplied to them.

Note also that symmetry of the dissipative bracket was crucial to recover OCRR. Recently, some arguments supporting the possibility of a nonsymmetric dissipative matrix were given [13]. Since the symmetry of the dissipative bracket was important to recover OCRR, we believe that the potential-based formulation of GENERIC, which becomes (2.15) for quadratic dissipation potentials, should be preferred to the forms with the nonsymmetric dissipative bracket.

Finally, note that OCRR provides insight into mathematical behavior of the linearized GENERIC; see Appendices B and C.

E. Geometrical interpretation of reversibility and irreversibility

The hitherto-derived results can be formulated more rigorously within differential geometry. Generally, an evolution equation is an equality between the time derivative of state variables and a vector field on a tangent bundle of the manifold [14] of state variables $\mathcal{M}$, i.e.,

$$\frac{d\mathbf{x}}{dt} = V^i(\mathbf{x})\frac{\partial}{\partial x^i} = \mathcal{V}(\mathbf{x}), \tag{2.33}$$

where state variables were denoted as coordinates $\mathbf{x}$. Note that we use Einstein's summation convention in this section. Time-reversal transformation $\mathbf{I}$ provides a diffeomorphism of manifold $\mathcal{M}$ to itself. This diffeomorphism then induces a push-forward of the vector field on the right-hand side of Eq. (2.33),

$$\mathbf{I}_\star\left(V^i\frac{\partial}{\partial x^i}\right) = \frac{\partial \mathbf{I}^i}{\partial x^j}(\mathbf{x})V^j(\mathbf{x})\frac{\partial}{\partial \mathbf{I}(\mathbf{x})^i}. \tag{2.34}$$

This push-forward then acts on Eq. (2.33) as follows:

$$\frac{d\mathbf{I}(\mathbf{x})}{d\tau} = -\mathbf{I}_\star\mathcal{V}|_{\mathbf{I}(\mathbf{x})}, \tag{2.35}$$

where dt was replaced by $-d\tau$ as in Definition 3. Definition 3 can be then reformulated as follows:

Definition 6. Vector field $\mathcal{V}$ is called reversible if and only if the push-forward only adds a minus sign in front of the vector field,

$$\boxed{\mathbf{I}_\star\mathcal{V} = -\mathcal{V}|_{\mathbf{I}(\mathbf{x})}}. \tag{2.36}$$

Roughly speaking, it means that all "arrows" along integral curves of the vector field are inverted if TRT is applied on the state variables. Recall that in the sense of Definition 3 the reversible part of the right-hand side of the evolution equation keeps the same form as the left-hand side with respect to TRT and that a minus sign is added in front of the left-hand side due to transformation of dt to $d\tau$. This is the minus sign which appears on the right-hand side of Eq. (2.36). Therefore, both definitions of reversibility 3 and 6 are equivalent.

Lemma 2. Definitions of reversibility 3 and 6 are equivalent.

Definition 6 is, however, more rigorous since it is formulated as a differential geometric identity (2.36).

Let us now formulate conditions (2.25), which ensured that the Poisson and dissipative brackets generate only reversible and irreversible evolution in the sense of Definition 3 geometrically. Assume, therefore, as well as in the derivation of the conditions, that all state variables have definite parities. That means that TRT acts on state variables as follows:

$$\mathbf{I}(\mathbf{x})^i = P(x^i)x^i. \tag{2.37}$$

The Jacobi matrix of this transformation is then

$$\frac{\partial \mathbf{I}(\mathbf{x})^i}{\partial x^j} = P(x^i)\delta^i_j, \tag{2.38}$$

where δ is the Kronecker delta. The Poisson vector field, which generates the reversible evolution, can be expressed as

$$\mathcal{V} = L^{ij}(\mathbf{x})\frac{\partial E}{\partial x^j}\frac{\partial}{\partial x^i}, \tag{2.39}$$

where summation stands generally for the scalar product and indices i and j may be also continuous as within the Boltzmann equation in Sec. III E. Condition (2.36) can be then rewritten as

$$L^{ij}|_{\mathbf{I}(\mathbf{x})} = -P(x^i)P(x^j)L^{ij}|_{\mathbf{x}}, \tag{2.40}$$

which is the geometrical interpretation of relation (2.25a).

But does any Poisson bracket satisfy this relation? To the best of our knowledge this is an open problem. All the examples of Poisson brackets formulated in this paper satisfy the relation, and we suppose that it is generally valid. To prove that, however, one would have to formulate how a Poisson bracket on a level of description can generally be inherited from a Poisson bracket on the most microscopic level of description, e.g., from the Hamiltonian dynamics, because TRT on the more macroscopic level is inherited from TRT on the most microscopic level and the Poisson bracket on the most microscopic level is reversible (Hamiltonian dynamics is reversible). A method of how to obtain a Poisson bracket on the more macroscopic level from the Poisson bracket of Hamiltonian dynamics by projection operators was formulated by H. C. Öttinger [15], and it is easy to show that any Poisson bracket obtained by use of this method fulfills relation (2.40) and thus is reversible. Nevertheless, the validity of the Jacobi identity for the Poisson bracket has not been derived in general and hence one cannot regard the method as generally valid yet.

In summary, it is still an open problem to show that any Poisson bracket on any level of description fulfills relation (2.36), and it is still necessary to prove that any Poisson bracket generates only reversible evolution. If the projection operator method [15] of construction of Poisson bracket on a more macroscopic level of description turned out to be generally valid, the problem would be solved since Poisson brackets constructed by the method automatically satisfy condition (2.40). Moreover, it can be shown by means of a quantum master equation that condition (2.40) is satisfied at least at equilibrium; see Sec. III D.

Analogically to the reversible evolution, irreversible evolution is generated by a vector field which is invariant to the push-forward $\mathbf{I}_\star$ induced by TRT. This leads to the following definition:

Definition 7. A vector field generates irreversible evolution if the push-forward induced by TRT acts on the field as follows:

$$\boxed{\mathbf{I}_\star \mathcal{V} = \mathcal{V}|_{\mathbf{I}(\mathbf{x})}}. \tag{2.41}$$

Therefore, if all state variables have definite parity, a condition analogical to (2.40) holds also for the $\mathbf{M}$ matrix,

$$M^{ij}|_{\mathbf{I}(\mathbf{x})} = +P(x^i)P(x^j)M^{ij}|_{\mathbf{x}}, \tag{2.42}$$

which is the geometrical interpretation of relation (2.25b).

In the more general setting where irreversible evolution is described by dissipation potential instead of dissipative matrix, the irreversible part of evolution equations transforms as follows:

$$\begin{aligned}
&\mathbf{I}_\star\left(\frac{\partial \Xi}{\partial \frac{\partial S}{\partial x^i}}\frac{\partial}{\partial x^i}\right)\\
&= \frac{\partial \mathbf{I}^i}{\partial x^j}\frac{\partial \Xi}{\partial \frac{\partial S}{\partial x^j}}\bigg|_{\mathbf{x}}\frac{\partial}{\partial \mathbf{I}^i(\mathbf{x})} = \frac{\partial \mathbf{I}^i}{\partial x^j}\frac{\partial \Xi}{\partial \frac{\partial S}{\partial \mathbf{I}^k}\frac{\partial \mathbf{I}^k}{\partial x^j}}\bigg|_{\mathbf{x}}\frac{\partial}{\partial \mathbf{I}^i(\mathbf{x})}\\
&= \frac{\partial \mathbf{I}^i}{\partial x^j}\frac{\partial \Xi}{\partial \frac{\partial S}{\partial \mathbf{I}^l}}\frac{\partial \frac{\partial S}{\partial \mathbf{I}^l}}{\partial \frac{\partial S}{\partial \mathbf{I}^k}\frac{\partial \mathbf{I}^k}{\partial x^j}}\bigg|_{\mathbf{x}}\frac{\partial}{\partial \mathbf{I}^i(\mathbf{x})} = \frac{\partial \mathbf{I}^i}{\partial x^j}\frac{\partial \Xi}{\partial \frac{\partial S}{\partial \mathbf{I}^l}}\frac{\partial x^j}{\partial \mathbf{I}^k}\delta^k_l\bigg|_{\mathbf{x}}\frac{\partial}{\partial \mathbf{I}^i(\mathbf{x})}\\
&= \frac{\partial \Xi}{\partial \frac{\partial S}{\partial \mathbf{I}^i(\mathbf{x})}}\frac{\partial}{\partial \mathbf{I}^i(\mathbf{x})},
\end{aligned} \tag{2.43}$$

because both dissipation potential and entropy are even under TRT in accordance with Assumption 2. We have thus proven the following lemma:

Lemma 3. Any even dissipation potential satisfies relation (2.36) and thus generates only irreversible evolution.

Note that the dissipation potential (as a function on manifold $\mathcal{M}$) is even if it is not altered by the push-forward induced by TRT.

In summary, it is still an open problem to prove that any Poisson bracket generates only reversible evolution, i.e., that relation (2.36) holds for the vector field generated by the bracket. On the other hand, any even dissipation potential automatically satisfies the condition for irreversible evolution (2.41). Since we are not aware of any Poisson bracket inconsistent with relation (2.36) and of any noneven dissipation potential, we believe that all the definitions of reversibility (3, 4, 5, and 6) are equivalent.

F. Nonentropic dissipation and time-reversal non-Hamiltonian dynamics

We have assumed so far that the mesoscopic time evolution describing an approach to a more macroscopic level of description is the time evolution generated by the abstract GENERIC equation described above. However, this is not true in general. We shall present below some well-known examples of non-GENERIC mesoscopic time evolution. Before doing so, we note that there are essentially two strategies for dealing with such dynamics. First is to relax the stringent GENERIC structure presented above in this paper. The second is then to regard the non-GENERIC time evolution as a reduced or an incomplete version of the GENERIC time evolution formulated on a more microscopic level of description. The first strategy is followed by Hütter *et al.* [13] and by Öttinger [15] by allowing, for instance, nonsymmetric dissipative bracket. We follow the second strategy. We present a few examples and then arguments in favor of our approach.

First, we present two examples of Hamiltonian dynamics with, as it is called by Villani [16], nonentropic dissipation. The first is, of course, the Hamiltonian mechanics of N particles ($N \sim 10^{23}$) composing isolated macroscopic systems. Experimental observations show that this time evolution approaches thermodynamic equilibrium states at which the behavior is seen to be described well by the classical equilibrium thermodynamics. The main objective of nonequilibrium statistical mechanics is to reformulate this dynamics into a dynamics in which this feature of solutions is manifestly displayed as an entropic dissipation. The mathematical rigorosity of such reformulations still remains inadequate.

Another example of the similar type has been, however, recently [16] investigated using complete mathematical rigor. The Hamiltonian time evolution in this example is generated by the Vlasov kinetic equation [16,17] describing the time evolution of macroscopic systems with long-range interactions (e.g., Coulomb interactions). No dissipative term is present in the Vlasov equation, and the Boltzmann entropy is conserved. It is nevertheless well known [16,18] that solutions to the Vlasov equation experience the so-called Landau damping. We thus have another example of the time evolution equation with nonentropic dissipation. We conjecture that the Vlasov kinetic equation can be approximately reformulated (with a rigorous meaning and control of the approximation) into an equation displaying manifestly the Landau damping as an entropic dissipation with an appropriately chosen entropy.

The next example is the feature of solutions of the Navier-Stokes equations (i.e., equations possessing the GENERIC structure described in this paper), known as the Kolmogorov energy cascade, emerging in turbulent flows. The passage of energy from large to small vortices described by the Kolmogorov cascade is a degradation of energy that is not seen in entropy production. Öttinger has suggested recently [19] to include this dynamics into GENERIC by allowing nonsymmetric irreversible brackets. Following the spirit of the previous two examples we suggest reformulating the Navier-Stokes equation into an equation in which the Kolmogorov energy cascade appears as an entropic dissipation. Such a reformulation is an interesting challenge.

In the next example we illustrate dynamics with irreversible time evolution that is not Hamiltonian. It is the time evolution equation that involves a "slip." Contrary to the previous example, the way such non-GENERIC equations are related to the abstract GENERIC is well understood and illustrated in detail in many examples. The macroscopic physical systems in which the time evolution equations with slip arise are suspensions of particles in a simple fluid whose time evolution is governed by the classical fluid mechanics. The suspended particles can be of various shapes, deformable or not deformable, and, for example, macromolecular chains. If the particles are passively advected (or, in other words, Lie dragged) with the fluid then the GENERIC structure of the simple fluid can be easily extended to the GENERIC structure of the suspension (we recall that in the Hamiltonian part it is though the concept of semidirect product [20]). But, in reality, the particles are not passively advected and, depending on the physics taking place on the particle-fluid interface, a "slip" occurs in the advection. With the slip, the time evolution is no longer GENERIC (in the sense of this paper); it involves a time-reversible term that is not Hamiltonian. But if we take into account the physics of the particle-fluid interface by lifting the formulation of the dynamics into a larger space in which another fluid velocity, namely the fluid velocity on the particle-fluid interface, is adopted as an independent state variable, then the dynamics becomes again GENERIC. The slip in this lifted formulation appears as a true dissipative term involving the extra velocity state variable. The original non-GENERIC time evolution equation with the slip is then a reduced version of the lifted GENERIC dynamics in which the extra velocity state variable has been eliminated by considering its time evolution as fast and by limiting ourselves to the stage in which its time evolution has already been completed. This procedure has been explicitly illustrated in the finite-dimensional version of GENERIC [21], in polymeric fluids [22], and in suspensions of rigid spheres [23] (i.e., in the context of the Smoluchowski equation).

Regarding another relaxation of the GENERIC structure with nonsymmetric irreversible brackets proposed by Öttinger [15], we shall see in Sec. III E that GENERIC with dissipation potential (i.e., GENERIC structure discussed in this paper) allows us to formulate the Boltzmann collision term as well as the time evolution equations arising in chemical kinetics.

Finally, we collect the arguments supporting our decision to insist on the GENERIC structure described above in this paper. First, it is the physics. The role of statistical mechanics is to regard macroscopic systems on a hierarchy of levels of description. Such levels are then related by a dissipative dynamics possessing the GENERIC structure an involving a appropriately chosen entropy. In the case of the slip, the physics responsible for it is the true dissipation (the friction) involving the fluid velocity on the particle-fluid interface. There is absolutely no problem in seeing the time evolution equations with the slip as reduced versions of true GENERIC equations in which the physics that is behind the slip is explicitly expressed. This completely fits the multiscale approach to mesoscopic physics that is absolutely inevitable in particular when dealing with complex systems arising in biophysics and nanotechnology.

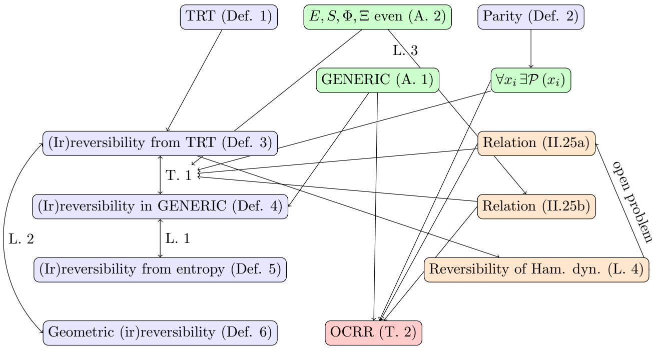

FIG. 1. (Color online) Conceptual map of this paper. The abbreviation L. stands for lemma, T. for theorem, and A. for assumption.

Besides the physical reasons in favor of the stringent GENERIC structure, there is also an obvious mathematical reason. The right-hand side of the abstract GENERIC equation is a sum of two terms. Is such a split unique? If we relax the requirements on the two terms, the answer is certainly negative. Indeed, for example, in the linearized GENERIC, one would not be able to reconstruct the **L** and **M** matrices from the **K** matrix if the requirement of symmetry of **M** and antisymmetry of **L** were dropped. Also the possibility to formulate the stringent GENERIC time evolution as a contact structure preserving dynamics with a deep thermodynamic meaning [9] supports our approach.

G. Conceptual map

For the reader's convenience we have included a conceptual map of this paper (Fig. 1).

III. ILLUSTRATIONS

The preceding results and in particular Theorem 2 are demonstrated in Hamiltonian dynamics, classical hydrodynamics, the theory of mixtures within CIT, the quantum master equation, and the Boltzmann equation.

A. Hamiltonian mechanics

Hamiltonian mechanics is easily formulated within GENERIC if we choose the following building blocks:

(i) state variables: positions and momenta of all particles $(\mathbf{q}_i, \mathbf{p}_i)$

(ii) Poisson bracket: the canonical Poisson bracket

$$\mathbf{L} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \tag{3.1}$$

(iii) Dissipative bracket: zero.

Evolution of the state variables then can be written as

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial E}{\partial \mathbf{p}_i}, \tag{3.2a}$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial E}{\partial \mathbf{q}_i}, \tag{3.2b}$$

which are just the standard Hamilton's equations.

Since the matrix $\mathbf{L}$ is constant (and thus even with respect to TRT), Theorem 2 applies also out of the near-equilibrium regime. In other words, coupling between $\mathbf{q}_i$ and $\mathbf{p}_i$ is always antisymmetric (since both the state variables have opposite parities). This is obviously correct for Hamilton's equations. In summary, OCRR imply that coupling between positions and momenta of particles is antisymmetric, which is compatible with the structure Hamilton's canonical equations.

Let us now reformulate the notion of reversibility geometrically. Evolution equation (3.2) is generated by the vector field

$$\mathcal{V} = \frac{\partial E}{\partial p}\frac{\partial}{\partial q} - \frac{\partial E}{\partial q}\frac{\partial}{\partial p}. \tag{3.3}$$

The push-forward acts on this vector field as follows:

$$\begin{aligned} \mathbf{I}_\star\left(\frac{\partial E}{\partial p}\frac{\partial}{\partial q} - \frac{\partial E}{\partial q}\frac{\partial}{\partial p}\right) &= \frac{\partial E}{\partial p}\frac{\partial}{\partial \mathbf{I}(q)} + \frac{\partial E}{\partial q}\frac{\partial}{\partial \mathbf{I}(p)} \\ &= -\left[\frac{\partial E}{\partial \mathbf{I}(p)}\frac{\partial}{\partial \mathbf{I}(q)} - \frac{\partial E}{\partial \mathbf{I}(q)}\frac{\partial}{\partial \mathbf{I}(p)}\right], \end{aligned} \tag{3.4}$$

which means that transforming state variables via TRT only inverts the sign of the Hamiltonian vector field, which is thus considered reversible in accordance with Definition 6.

Moreover, it is shown in Appendix A that any Poisson bracket on the level of description of Hamiltonian dynamics, which has to be obtained from the canonical bracket by transformation of coordinates since it expresses the same evolution, also generates only reversible evolution.

Having established the time reversibility of the particle Hamiltonian dynamics we bring into attention another result obtained in this dynamics that while the time evolution is, strictly speaking, reversible, it is "practically" irreversible. The result, obtained by Henri Poincaré [24], is the sensitive dependence of the trajectories on the initial conditions. According to this result, the separation among most trajectories grows exponentially. This means that however small the initial perturbation (due to, for instance, a numerical inaccuracy in computing or an incomplete isolation from exterior influences in experimental observations), the trajectory followed after inversion of time will not retrace the trajectory followed before the inversion. This result most certainly plays an important role in the emergence of the explicit time irreversibility seen in mesoscopic observations. A closer investigation of this problem is beyond the scope of this paper.

B. Classical hydrodynamics

Theorem 2 can be also illustrated on classical hydrodynamics [8], where state variables are [25] density field $\rho(\mathbf{r})$, field of momentum density $\mathbf{u}(\mathbf{r})$, and field of internal energy density $\epsilon(\mathbf{r})$. The energy of the whole system is specified as

$$E = \int_V \frac{\mathbf{u}(\mathbf{r})^2}{2\rho(\mathbf{r})} + \epsilon(\mathbf{r})\, d\mathbf{r}. \tag{3.5}$$

The entropy of the whole system is given by

$$S = \int_V s(\epsilon(\mathbf{r}),\rho(\mathbf{r}))\, d\mathbf{r}. \tag{3.6}$$

Poisson bivector is [8]

$$L(\mathbf{r},\mathbf{r}') = \begin{bmatrix} 0 & \rho(\mathbf{r}')\frac{\partial\delta}{\partial\mathbf{r}'} & 0 \\ -\rho(\mathbf{r})\frac{\partial\delta}{\partial\mathbf{r}} & \mathbf{u}(\mathbf{r}')\frac{\partial\delta}{\partial\mathbf{r}'} - \frac{\partial\delta}{\partial\mathbf{r}}\mathbf{u}(\mathbf{r}) & -\epsilon(\mathbf{r})\frac{\partial\delta}{\partial\mathbf{r}} + \frac{\partial\delta}{\partial\mathbf{r}'}p(\mathbf{r}') \\ 0 & \epsilon(\mathbf{r}')\frac{\partial\delta}{\partial\mathbf{r}'} - \frac{\partial\delta}{\partial\mathbf{r}}p(\mathbf{r}) & 0 \end{bmatrix}, \tag{3.7}$$

where $\delta = \delta(\mathbf{r}-\mathbf{r}')$ and δ denotes Dirac distribution [26]. The dissipative bracket is specified as [8]

$$M(\mathbf{r},\mathbf{r}') = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \left(\frac{\partial}{\partial\mathbf{r}'}\frac{\partial}{\partial\mathbf{r}} + \mathbf{1}\frac{\partial}{\partial\mathbf{r}'}\cdot\frac{\partial}{\partial\mathbf{r}}\right)\eta T\delta + 2\frac{\partial}{\partial\mathbf{r}}\frac{\partial}{\partial\mathbf{r}'}\hat{k}T\delta & \frac{\partial}{\partial\mathbf{r}}\cdot\eta T\dot{\gamma}\delta + \frac{\partial}{\partial\mathbf{r}}\hat{k}T\mathrm{tr}\dot{\gamma}\delta \\ 0 & \frac{\partial}{\partial\mathbf{r}'}\cdot\eta T\dot{\gamma}\delta + \frac{\partial}{\partial\mathbf{r}'}\hat{k}T\mathrm{tr}\dot{\gamma}\delta & \frac{1}{2}\eta T\dot{\gamma}:\dot{\gamma}\delta + \frac{\partial}{\partial\mathbf{r}}\cdot\frac{\partial}{\partial\mathbf{r}'}\lambda T^2\delta + \frac{1}{2}\hat{k}T\mathrm{tr}\dot{\gamma}^2\delta \end{bmatrix}, \tag{3.8}$$

where $\dot{\gamma}$ is the symmetric gradient of velocity field, η is the shear viscosity, $\hat{k}$ is the bulk viscosity, and λ is the thermal conductivity.

The Poisson matrix (3.7) is obviously antisymmetric with respect to simultaneous transposition and swapping arguments $\mathbf{r}$ and $\mathbf{r}'$. Hydrodynamic state variables have the following parities:

$$\mathcal{P}(\rho) = 1, \qquad \mathcal{P}(\mathbf{u}) = -1, \qquad \mathcal{P}(\epsilon) = 1. \tag{3.9}$$

It can be easily checked that parities of the Poisson matrix are

$$\mathcal{P}(\mathbf{L}) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & -1 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \tag{3.10}$$

which is in agreement with result (2.25a), and the Poisson bracket generates reversible evolution, consequently.

Dissipative matrix is obviously symmetric with respect to transposition and swapping arguments $\mathbf{r}$ and $\mathbf{r}'$. The matrix has the following parities:

$$\mathcal{P}(\mathbf{M}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & -1 & 1 \end{pmatrix}, \tag{3.11}$$

which is in agreement with the result (2.25b) as well, and thus the dissipative bracket generates irreversible evolution.

Hitherto, we have shown that classical hydrodynamics is consistent with relations (2.25). Let us now show how the results of the near-equilibrium treatment apply to classical hydrodynamics. To do so we substitute equilibrium values of state variables, $(\rho_{\text{th}}, 0, \varepsilon_{\text{th}})$, into both matrices. Since the system is considered isolated, the equilibrium value of momentum is zero everywhere. This way the Poisson matrix simplifies to

$$L(x_{\text{th}})(\mathbf{r},\mathbf{r}') = \begin{pmatrix} 0 & \rho_{\text{th}} \frac{\partial \delta}{\partial \mathbf{r}'} & 0 \\ -\rho_{\text{th}} \frac{\partial \delta}{\partial \mathbf{r}} & 0 & -\epsilon_{\text{th}} \frac{\partial \delta}{\partial \mathbf{r}} + \frac{\partial \delta}{\partial \mathbf{r}'} p_{\text{th}} \\ 0 & \epsilon_{\text{th}} \frac{\partial \delta}{\partial \mathbf{r}'} - \frac{\partial \delta}{\partial \mathbf{r}} p_{\text{th}} & 0 \end{pmatrix}, \tag{3.12}$$

and the dissipative matrix simplifies to

$$M(x_{\text{th}})(\mathbf{r},\mathbf{r}') = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \left(\frac{\partial}{\partial \mathbf{r}'} \frac{\partial}{\partial \mathbf{r}} + \mathbf{1} \frac{\partial}{\partial \mathbf{r}'} \cdot \frac{\partial}{\partial \mathbf{r}}\right) \eta T \delta + 2 \frac{\partial}{\partial \mathbf{r}} \frac{\partial}{\partial \mathbf{r}'} \hat{k} T \delta & 0 \\ 0 & 0 & \frac{\partial}{\partial \mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{r}'} \lambda T^2 \delta \end{bmatrix}. \tag{3.13}$$

It can be easily checked that terms corresponding to state variables with the same parities have vanished in the Poisson matrix while terms corresponding to state variables with different parities have vanished in the dissipative matrix. Therefore, OCRR are fulfilled for near-equilibrium classical hydrodynamics, which is the result of Theorem 2, proof of which we have just retraced. Near-equilibrium evolution equations are derived below in this section.

We have thus shown validity of OCRR near the global equilibrium. But classical hydrodynamics (and the whole CIT) is based on the assumption of local equilibrium only. Are OCRR valid for local equilibrium as well? To answer the question one would at first have to specify the meaning of OCRR in a regime not near the global equilibrium. If the meaning were that coupling of state variables with the same parities is symmetric while coupling of state variables with different parities is antisymmetric, then OCRR are clearly violated in the regime. Indeed, the dissipative matrix (3.8) provides symmetric coupling between momentum and energy, which have opposite parities. On the other hand, if the coupling coefficients (e.g., coefficient of thermodiffusion in CIT [6,27]) are constant, that is, the same as in equilibrium, coupling keeps its symmetricity or antisymmetricity also out of the near-global-equilibrium regime. In summary, one should bear in mind that OCRR are valid near the global equilibrium and that GENERIC is the far-from-equilibrium extension of OCRR, which may have the same symmetry or antisymmetry as the near-global equilibrium also far from equilibrium.

Let us now introduce deviations of hydrodynamic state variables from their equilibrium values $\tilde{\rho}$, $\tilde{\mathbf{u}}$ and $\tilde{\epsilon}$. Evolution equations for these state variables can be inferred from the general near-equilibrium evolution equation (2.28). Second derivatives of thermodynamic potential Φ, which is constructed according to formula (2.17), are

$$\left.\frac{\partial^2 \Phi}{\partial \rho \partial \rho}\right|_{\text{th}} = \left.\left(\frac{\partial \mu / T}{\partial \rho}\right)_{\epsilon}\right|_{\text{th}}, \qquad \left.\frac{\partial^2 \Phi}{\partial \rho \partial u_i}\right|_{\text{th}} = 0, \qquad \left.\frac{\partial^2 \Phi}{\partial \rho \partial \epsilon}\right|_{\text{th}} = \left.\left(\frac{\partial \mu / T}{\partial \epsilon}\right)_{\rho}\right|_{\text{th}}, \tag{3.14a}$$

$$\left.\frac{\partial^2 \Phi}{\partial u_i \partial \rho}\right|_{\text{th}} = 0, \left.\frac{\partial^2 \Phi}{\partial u_i \partial u_i}\right|_{\text{th}} = \frac{\delta_{ij}}{\rho_{\text{th}} T_{\text{th}}}, \qquad \left.\frac{\partial^2 \Phi}{\partial u_i \partial \epsilon}\right|_{\text{th}} = 0, \tag{3.14b}$$

$$\left.\frac{\partial^2 \Phi}{\partial \epsilon \partial \rho}\right|_{\text{th}} = -\left.\left(\frac{\partial T^{-1}}{\partial \rho}\right)_{\epsilon}\right|_{\text{th}}, \qquad \left.\frac{\partial^2 \Phi}{\partial \epsilon \partial u_i}\right|_{\text{th}} = 0, \qquad \left.\frac{\partial^2 \Phi}{\partial \epsilon \partial \epsilon}\right|_{\text{th}} = -\left.\left(\frac{\partial T^{-1}}{\partial \epsilon}\right)_{\rho}\right|_{\text{th}}. \tag{3.14c}$$

Note that $\frac{\partial^2 \Phi}{\partial \epsilon \partial \rho}|_{\text{th}} = \frac{\partial^2 \Phi}{\partial \rho \partial \epsilon}|_{\text{th}}$ due to Maxwell's relations. Plugging relations (3.14) into (2.30), thermodynamic forces become

$$X_\rho = \left.\left(\frac{\partial \mu / T}{\partial \rho}\right)_{\epsilon}\right|_{\text{th}} \tilde{\rho} + \left.\left(\frac{\partial \mu / T}{\partial \epsilon}\right)_{\rho}\right|_{\text{th}} \tilde{\epsilon}, \tag{3.15a}$$

$$X_{u_i} = \frac{\tilde{u}_i}{\rho_{\text{th}} T_{\text{th}}}, \tag{3.15b}$$

$$X_\epsilon = -\left.\left(\frac{\partial T^{-1}}{\partial \rho}\right)_{\epsilon}\right|_{\text{th}} \tilde{\rho} - \left.\left(\frac{\partial T^{-1}}{\partial \epsilon}\right)_{\rho}\right|_{\text{th}} \tilde{\epsilon}. \tag{3.15c}$$

The matrix K_{ij} is constructed from equilibrium Poisson bracket (3.12) and dissipative bracket (3.13) according to (2.28). It can be easily seen that the matrix becomes

$$\mathbf{K}(\mathbf{r},\mathbf{r}') = \begin{pmatrix} 0 & T_{\text{th}} \rho_{\text{th}} \frac{\partial \delta}{\partial r_i'} & 0 \\ -T_{\text{th}} \rho_{\text{th}} \frac{\partial \delta}{\delta r_i} & K_{u_i u_j}(\mathbf{r},\mathbf{r}') & -T_{\text{th}} \epsilon_{\text{th}} \frac{\partial \delta}{\partial r_i} + T_{\text{th}} p_{\text{th}} \frac{\partial \delta}{\partial r_i'} \\ 0 & T_{\text{th}} \epsilon_{\text{th}} \frac{\partial \delta}{\partial r_i'} - \frac{\partial \delta}{\partial r_i} T_{\text{th}} p_{\text{th}} & -\frac{\partial}{\partial r_i} \frac{\partial}{\partial r_i'} \left(\lambda_{\text{th}} T_{\text{th}}^2 \delta\right) \end{pmatrix}, \tag{3.16}$$

where

$$K_{u_i u_j}(\mathbf{r},\mathbf{r}') = -\left(\frac{\partial}{\partial r'_i}\frac{\partial}{\partial r_j} + \delta_{ij}\frac{\partial}{\partial r'_k}\frac{\partial}{\partial r_k}\right)(\eta_{\text{th}}T_{\text{th}}\delta) - 2\frac{\partial}{\partial r_i}\frac{\partial}{\partial r'_j}(\hat{k}_{\text{th}}T_{\text{th}}\delta). \tag{3.17}$$

Onsager-Casimir reciprocal relations can be now interpreted as follows. Matrix $K_{ij}(\mathbf{r},\mathbf{r}')$ provides coupling between state variables. Variables $\tilde{\rho}$ and $\tilde{\epsilon}$ are not coupled since the corresponding terms in the matrix are zero. On the other hand, variables $\tilde{\rho}(\mathbf{r})$ and $\tilde{u}_i(\mathbf{r}')$ have opposite parities and are coupled through the second term in the first row and the first term in the second row. The terms are the same form except for sign, which means that the coupling is antisymmetric. This is in agreement with that $\mathcal{P}(\tilde{\rho}) = -\mathcal{P}(\tilde{u_i})$. Similarly, coupling between $\tilde{u}_i(\mathbf{r})$ and $\tilde{\epsilon}(\mathbf{r}')$, which also have opposite parities, is antisymmetric as well. On the other hand, variables $u_i(\mathbf{r})$ and $u_j(\mathbf{r}')$ have the same parity (they are both odd) and they are coupled through the $K_{u_i u_j}(\mathbf{r},\mathbf{r}')$ term, which is symmetric. In summary, coupling between variables with the same parity is symmetric while coupling between variables with opposite parities is antisymmetric. The symmetric coupling is given by the dissipative bracket while the antisymmetric coupling is given by the Poisson bracket. This is exactly the statement of Theorem 2, which has hereby been demonstrated on classical hydrodynamics.

Finally, evolution equations for the near equilibrium state variables can be constructed as (2.28). The evolution equation for $\tilde{\rho}$ is given by

$$\frac{\partial \tilde{\rho}(\mathbf{r})}{\partial t} = \int_V \sum_i K_{\rho u_i}(\mathbf{r},\mathbf{r}')X_{u_i}(\mathbf{r}')\,d\mathbf{r}'. \tag{3.18}$$

Other evolution equations can be constructed analogically. After some algebra we obtain

$$\frac{\partial \tilde{\rho}}{\partial t} = -\text{div}\tilde{\mathbf{u}}, \tag{3.19}$$

$$\frac{\partial \tilde{\mathbf{u}}}{\partial t} = -\nabla\tilde{p} + \frac{\eta_{\text{th}} + 2\hat{K}_{\text{th}}}{\rho_{\text{th}}}\nabla\text{div}\,\tilde{\mathbf{u}} + \frac{\eta_{\text{th}}}{\rho_{\text{th}}}\Delta\tilde{\mathbf{u}}, \tag{3.20}$$

$$\frac{\partial \tilde{\epsilon}}{\partial t} = -\frac{\epsilon_{\text{th}} + p_{\text{th}}}{\rho_{\text{th}}}\text{div}\,\tilde{\mathbf{u}} + \lambda_{\text{th}}\Delta\tilde{T}, \tag{3.21}$$

where

$$\nabla\tilde{p} \overset{\text{def}}{=} \left(\frac{\partial p}{\partial \rho}\right)_{\epsilon}\Bigg|_{\text{th}}\nabla\tilde{\rho} + \left(\frac{\partial p}{\partial \epsilon}\right)_{\rho}\Bigg|_{\text{th}}\nabla\tilde{\epsilon} \tag{3.22}$$

and

$$\Delta\tilde{T} \overset{\text{def}}{=} \left(\frac{\partial T}{\partial \rho}\right)_{\epsilon}\Bigg|_{\text{th}}\Delta\tilde{\rho} + \left(\frac{\partial T}{\partial \epsilon}\right)_{\rho}\Bigg|_{\text{th}}\Delta\tilde{\epsilon}. \tag{3.23}$$

Note that evolution equations (3.19)–(3.21) can be treated within near-equilibrium statistical physics. Indeed, the standard statistical proof of OCRR [6] applies to the near-equilibrium evolution. Moreover, these equations can be directly used in the fluctuating hydrodynamics framework [28] and the fluctuation-dissipation theorem can be applied, consequently.

In summary, we have shown that Theorem 2 is valid within classical hydrodynamics. We have also linearized classical hydrodynamics so OCRR are revealed explicitly.

C. Theory of mixtures within CIT

Let us now analyze OCRR within the theory of mixtures developed in CIT [6]. The theory has been reformulated within GENERIC [27] without chemical reactions. At first we verify that Theorem 2 holds also in this case and, consequently, we try to extend formulation of the theory [27] so it contains coupling between chemical reactions with isotropic viscous stress [6]. Note that many details which can be found in the original paper [27] are skipped to avoid repetition.

Let us at first analyze the Poisson bracket of CIT [27]. For simplicity, we do not reproduce the Poisson bracket here but it can be found in Eq. (32) of the original paper [27]. When evaluating the Poisson bracket at equilibrium, only the term

$$-\int u_\alpha\left(\frac{\partial A}{\partial u_\alpha}\frac{\partial}{\partial r_\beta}\frac{\partial B}{\partial u_\beta} - \frac{\partial B}{\partial u_\gamma}\frac{\partial}{\partial r_\beta}\frac{\partial A}{\partial u_\beta}\right)d\mathbf{r} \tag{3.24}$$

disappears since $\mathbf{u} = 0$ at equilibrium. All the remaining terms in the Poisson bracket provide coupling between even and odd variables, and we can, therefore, conclude that the Poisson bracket is responsible for coupling variables of different parities near equilibrium. This is in agreement with Theorem 2.

Similarly, only the terms coupling internal energy and momentum disappear from the dissipative bracket (44) of the paper [27], and the dissipative bracket is responsible for coupling variables with the same parity near equilibrium, which is again in agreement with Theorem 2.

Let us now analyze the possibility of coupling between the isotropic viscous stress and reaction rate. The energy (no potential energy is considered) and entropy (in accordance with Gibbs' definition [29]) of the mixture are specified as

$$E = \int \frac{\mathbf{u}^2}{2\rho} + \varepsilon(\mathbf{r})d\mathbf{r}, \quad S = \int s(\rho_1,\ldots,\rho_n,\rho,\varepsilon)d\mathbf{r}, \tag{3.25}$$

where $\rho_1,\ldots,\rho_n$ are densities of species $1,\ldots,n$, $\rho = \sum_{i=1}^n \rho_i$ is the total density, and ε is internal energy density. The following relations will be needed in the subsequent discussion:

$$\frac{\delta E}{\delta \rho_i} = 0, \quad \frac{\delta S}{\delta \rho_i} = -\frac{\mu_i}{T}, \tag{3.26}$$

$$\frac{\delta E}{\delta u_\gamma} = \frac{u_\gamma}{\rho}, \quad \frac{\delta S}{\delta u_\gamma} = 0. \tag{3.27}$$

Note that μ_i is the chemical potential of the i-th species and T is temperature.

For divergence of velocity to affect evolution equation of density ρ_i, the Poisson bracket needs to contain a term with $\frac{\delta A}{\delta u_\gamma}$ and $\frac{\delta B}{\delta \rho_i}$. Such a term is, however, already present in the bracket. In order to provide some extra influence, one needs to add a term,

$$-\sum_{i=1}^{n}\int L_i(\rho_1,\ldots,\rho_n,\rho,\mathbf{u},\varepsilon)\times\left(\frac{\delta A}{\delta u_\gamma}\frac{\partial}{\partial r_\gamma}\frac{\delta B}{\delta\rho_i}-\frac{\delta B}{\delta u_\gamma}\frac{\partial}{\partial r_\gamma}\frac{\delta A}{\delta\rho_i}\right)d\mathbf{r}, \tag{3.28}$$

where L_i is an unknown function of all state variables. Such an extended Poisson bracket would indeed provide the additional effect of divergence of velocity to evolution equations for $\rho_1,\ldots,\rho_n$, as can be straightforwardly verified. But is such coupling compatible with degeneracy conditions (2.16)? Evaluating the term (3.28) with a general functional A and entropy gives

$$-\sum_{i=1}^{n}\int L_i\frac{\delta A}{\delta u_\gamma}\frac{\partial}{\partial r_\gamma}\left(-\frac{\mu_i}{T}\right)d\mathbf{r}, \tag{3.29}$$

which generally differs from zero. Therefore, the term cannot be added to the Poisson bracket (without altering the well established Gibbs-Duhem relation for pressure) because it would violate the degeneracy condition. We can conclude that the effect of the isotropic viscous stress on partial density cannot be caused by the Poisson bracket within CIT since it would violate degeneracy conditions [30] (2.16).

Can the effect be caused by the dissipative bracket? To provide the coupling, one needs to add a term,

$$-\sum_{i=1}^{n}\int L_i(\rho_1,\ldots,\rho_n,\rho,\mathbf{u},\varepsilon)\times\left(\frac{\delta A}{\delta u_\gamma}\frac{\partial}{\partial r_\gamma}\frac{\delta B}{\delta\rho_i}+\frac{\delta B}{\delta u_\gamma}\frac{\partial}{\partial r_\gamma}\frac{\delta A}{\delta\rho_i}\right)d\mathbf{r}, \tag{3.30}$$

to the dissipative bracket. L_i is again an unknown function of all state variables. Let us check the degeneracy condition (2.16), taking into account the dissipative bracket. Evaluating the term (3.30) with a general functional A and energy gives

$$-\sum_{i}\int L_i\frac{u_\gamma}{\rho}\frac{\partial}{\partial r_\gamma}\frac{\delta A}{\delta\rho_i}d\mathbf{r}, \tag{3.31}$$

which again differs form zero generally. Therefore, such a term cannot be added to the dissipative bracket because it would violate the corresponding degeneracy condition.

In conclusion, the coupling between isotropic viscous stress and chemical reactions within CIT is not consistent with the GENERIC framework, and it should, therefore (as GENERIC can successfully be considered as a generalization of CIT), be regarded as an artifact of insufficient structure within the standard treatment of CIT [6,31,32].

On the other hand, it has been shown recently that coupling between mechanics and chemical reactions may successfully explain many phenomena in physics and chemistry [33,34], and this coupling is naturally formulated within GENERIC. In these works, however, rate of chemical reactions is among state variables. Such a new variable then can be coupled to mechanics consistently. From the thermodynamic point of view, these works use an idea similar to EIT when promoting reaction rate (or its conjugate) into a new state variable. Therefore, such thermodynamics is more general than CIT, and it admits coupling between chemistry and mechanics.

D. Master equation

In this section we discuss the relation between the quantum master equation and OCRR. There are many ways that the master equation can be derived and understood. A rather simple but physically transparent way was developed by van Kampen [35], where phase space was divided into phase cells and, instead of knowledge of probability of a system being in an exact state in the phase space, only the probability that the system is in a phase cell is available. Such coarse-graining is, in fact, a realization of two levels of description, the finer being the level where evolution is given by the Schrödinger equation [36] while the coarser level is the level where the probability that the system is in a particular phase cell is governed by a master equation.

The Schrödinger equation is reversible with respect to the TRT introduced in quantum theory [37]. This TRT, which transforms wave functions into their complex conjugates, is compatible with the notion of TRT from Sec. II A since it, for example, inverts momenta of particles [37].

Now introducing the phase cells according to van Kampen [35] and observing only probabilities that the system is in a phase cell, we define a new, more macroscopic, level of description. The probabilities are governed by the master equation

$$\frac{dP_i}{dt}=\sum_j W_{i,j}P_j, \tag{3.32}$$

where an explicit expression for the matrix $W_{i,j}$ is available [35]. Note that the matrix $W_{i,j}$ is supposed to be constant and that it does not need to be symmetric. For the probabilities to sum up to 1 for any set of probabilities, it holds that

$$\sum_i W_{i,j}=0. \tag{3.33}$$

Detailed balance can be expressed as [35]

$$W_{i,j}(\mathbf{H})G_j=W_{-j,-i}(-\mathbf{H})G_{-i}\quad G_i=G_{-i}\quad\forall i,j, \tag{3.34}$$

where the number of states in phase cell i was denoted by G_i. Phase cell $-i$ is defined so any observable dependent on velocities, i.e., represented by an imaginary operator, has a sign opposite that in cell i. On the other hand, even observables, which do not depend on velocities, i.e., are represented by real operators, have the same value within both cells i and $-i$. The intensity of the magnetic field was denoted by $\mathbf{H}$ but let us suppose for simplicity that it is zero hereafter.

Combining (3.33) and (3.34), it can be obtained that also

$$\sum_j W_{i,j}G_j=0. \tag{3.35}$$

The stationary (or equilibrium) probability distribution is obtained for the right-hand side of Eq. (3.32) equal to zero. Equation (3.35) then implies that the equilibrium distribution is given by a standard microcanonical probability distribution,

$$P_i=\frac{G_i}{G}, \tag{3.36}$$

where $G=\sum_j G_j$.

Let us now introduce deviations of probabilities from their equilibrium values,

$$\pi_i = P_i - \frac{G_i}{G}. \tag{3.37}$$

The master equation (3.32) can be reformulated equivalently as

$$\frac{d\pi_i}{dt} = \sum_j \underbrace{W_{ij}\frac{G_j}{G}}_{K_{ij}} \cdot \underbrace{\frac{G}{G_j}\pi_j}_{X_j}, \tag{3.38}$$

where matrix **K** and vector of thermodynamic forces **X** were introduced. Property (3.34) translates into

$$K_{i,j} = K_{-j,-i}. \tag{3.39}$$

This form of master equation can be identified with the general near-equilibrium evolution equation (2.28). Thermodynamic potential can be introduced naturally as

$$\Phi = -S + \frac{E}{k_B T} \tag{3.40}$$

with entropy and energy specified as

$$S = -\sum_i P_i \ln\frac{P_i}{G_i} \quad \text{and} \quad E = E\sum_i P_i, \tag{3.41}$$

where E is the energy of the energy shell which contains all the phase cells. The definition of thermodynamic forces from Eq. (3.38) is then compatible with (2.30), as can be verified straightforwardly. We have thus formulated the master equation within GENERIC.

Note that in the original work [35] it was entropy rather than thermodynamic potential that governed the evolution. But since entropy (3.41) was approximated by a quadratic function, difference between thermodynamic potential and entropy smears out. Replacing entropy with thermodynamic potential makes the master equation compatible with GENERIC.

Let us now analyze how TRT acts on the master equation. TRT inverts velocities and since cell $-i$ corresponds to cell i with inverted velocities of particles (see the original paper [35] for more details and proper quantum-mechanical interpretation), we have that $\mathbf{I}(P_j) = P_{-j}$ and hence (using the fact that W_{ij} are constant)

$$\mathbf{I}(G_j) = G_{-j} = G_j, \quad \mathbf{I}(K_{ij}) = \mathbf{I}\left(W_{ij}\frac{G_j}{G}\right) = K_{ij},$$
$$\mathbf{I}(\pi_j) = \mathbf{I}\left(P_i - \frac{G_i}{G}\right) = \pi_{-j}, \quad \mathbf{I}(X_j) = \mathbf{I}\left(\frac{G}{G_j}\pi_j\right) = X_{-j}.$$

Therefore Eq. (3.38) is converted by the action of TRT into

$$\begin{aligned}\frac{d\pi_{-i}}{d\tau} &\overset{(3.38)}{=} \sum_j -K_{i,j}X_{-j} \overset{(3.39)}{=} \sum_j -K_{-j,-i}X_{-j}\\ &= \sum_{-j} K_{[-i,-j]}X_{-j} - \sum_j K_{(-i,-j)}X_{-j}.\end{aligned} \tag{3.42}$$

Since TRT converts π_i into π_{-i}, state variables π_i do not have definite parity. But state variables with definite parity A_α and B_β may be introduced as

$$A_\alpha = \sum_i A_{\alpha,i}\pi_i, \qquad A_{\alpha,i} = A_{\alpha,-i}, \tag{3.43}$$

$$B_\beta = \sum_i B_{\beta,i}\pi_i, \qquad B_{\beta,i} = -B_{\beta,-i}. \tag{3.44}$$

Note that constants A_α and B_β are not affected by TRT. These state variables are closer to experimental measurements than probabilities π_i, which are not usually available experimentally. Transformations (3.43) and (3.44) also affect thermodynamic forces, which are always given by definition (2.30). Thermodynamic forces in the new variables are, therefore, defined as

$$\tilde{X}_{\alpha'} = \sum_\alpha \left.\frac{\partial^2\Phi}{\partial A_{\alpha'}\partial A_\alpha}\right|_{\text{eth}} A_\alpha + \sum_\beta \left.\frac{\partial^2\Phi}{\partial A_{\alpha'}\partial B_\beta}\right|_{\text{eth}} B_\beta, \tag{3.45}$$

$$\tilde{X}_{\beta'} = \sum_\alpha \left.\frac{\partial^2\Phi}{\partial B_{\beta'}\partial A_\alpha}\right|_{\text{eth}} A_\alpha + \sum_\beta \left.\frac{\partial^2\Phi}{\partial B_{\beta'}\partial B_\beta}\right|_{\text{eth}} B_\beta. \tag{3.46}$$

These new forces are related to the old forces through

$$X_j = \sum_\alpha A_{\alpha,j}\tilde{X}_\alpha + \sum_\beta B_{\beta,j}\tilde{X}_\beta, \tag{3.47}$$

which follows easily from (3.43) and (3.44).

Master equation (3.38) can be also transformed into the new variables easily. For example, even variable $A_{\alpha'}$ is governed by

$$\begin{aligned}\frac{dA_{\alpha'}}{dt} &= \sum_{i,j} A_{\alpha',i}K_{ij}X_j\\ &= \sum_\alpha \underbrace{\sum_{i,j} A_{\alpha',i}K_{ij}A_{\alpha,j}}_{\tilde{K}_{\alpha',\alpha}}\tilde{X}_\alpha + \sum_\beta \underbrace{\sum_{i,j} A_{\alpha',i}K_{ij}B_{\beta,j}}_{\tilde{K}_{\alpha',\beta}}\tilde{X}_\beta.\end{aligned} \tag{3.48}$$

The evolution equation for $B_{\beta'}$ and the definitions of $\tilde{K}_{\alpha,\beta}$, $\tilde{K}_{\beta,\alpha}$, and $\tilde{K}_{\beta',\beta}$ are analogous.

Let us now find out what property (3.39) tells about the new matrix $\tilde{K}$. From the definition of the new matrix it follows that

$$\tilde{K}_{\alpha',\alpha} = \sum_{i,j} A_{\alpha',i}K_{i,j}A_{\alpha,j} = \sum_{i,j} A_{\alpha',i}K_{-j,-i}A_{\alpha,j} = \tilde{K}_{\alpha,\alpha'}, \tag{3.49}$$

$$\tilde{K}_{\alpha,\beta} = \sum_{i,j} A_{\alpha,i}K_{i,j}B_{\beta,j} = \sum_{i,j} A_{\alpha,i}K_{-j,-i}B_{\beta,j} = -\tilde{K}_{\beta,\alpha}. \tag{3.50}$$

In other words, matrix $\tilde{K}_{\alpha',\alpha}$, which provides coupling between two even variables, is symmetric while matrix $\tilde{K}_{\alpha,\beta}$, which provides coupling between an even and an odd variable, is antisymmetric. Analogously, matrix $\tilde{K}_{\beta',\beta}$ is also symmetric.

The antisymmetric part of matrix $\tilde{\mathbf{K}}$ can be, according to (2.29), regarded as a Poisson bivector which generates a

Poisson bracket, while the symmetric part represents the dissipative bracket. Moreover, the condition of detailed balance derived from quantum-mechanical considerations (3.39) then implies that state variables with the same parity are coupled via the symmetric dissipative matrix while state variables with opposite parities are coupled via the antisymmetric Poisson matrix near equilibrium, i.e., OCRR are fulfilled.

This is, in fact, the statement of Theorem 2. It can be also easily checked that all assumptions of Theorem 2 except for the fourth are fulfilled. The fourth assumption brings validity of relations (2.25). Therefore, we can invert meaning of the theorem [38] and conclude that we have proven that relations (2.25) are fulfilled at least at equilibrium. In summary, we have obtained full agreement between Theorem 2 and finite-dimensional dynamics [35], and we have shown that relations (2.25) are valid at least at equilibrium. To study validity of these relations in the far-from-equilibrium regime one would have to use a more general treatment than the near-equilibrium master equation presented here.

Is the evolution generated by the antisymmetric part of matrix $\tilde{\mathbf{K}}$ really reversible as it should if interpreted as a Poisson bivector? TRT applied on Eq. (3.48) gives

$$-\frac{dA_{\alpha'}}{d\tau} = \sum_{\alpha} \tilde{K}_{\alpha',\alpha}\tilde{X}_{\alpha} + \sum_{\beta} \tilde{K}_{\alpha',\beta}(-\tilde{X}_{\beta}), \tag{3.51}$$

where constantness of $\mathbf{K}$, $A_{\alpha,i}$, and $B_{\beta,i}$ was used. The part of the right-hand side with antisymmetric matrix $\tilde{K}_{\alpha',\beta}$ transforms in the same way as the left-hand side and so it represents reversible evolution. In other words, the antisymmetric part of matrix $\tilde{\mathbf{K}}$ generates reversible evolution while the symmetric part generates irreversible evolution. This is in accordance with that the antisymmetric part represents a Poisson bracket while the symmetric part represents a symmetric dissipation bracket (or dissipation potential).

Note also that passage to the more coarse level, where state variables are given by P_i instead of the full density matrix, introduces some dissipation described by the symmetric part of matrix $\tilde{\mathbf{K}}$, which is just a transformation of the symmetric part of matrix $\mathbf{K}$. Indeed, the Schrödinger equation is completely reversible while the master equation contains also irreversible evolution.

In summary, Theorem 2 is compatible with finite-dimensional dynamics governed by the quantum master equation [35]. After introducing state variables with parities, OCRR are revealed, and the transition matrix from the master equation can be regarded as a sum of a Poisson bracket and a dissipative bracket. Moreover, relations (2.25) are proven to be generally valid, at least at equilibrium.

E. Boltzmann equation

Let us illustrate Theorem 2 on the Boltzmann equation. State variables are given by the field of probability density $f(\mathbf{r},\mathbf{v})$. The Boltzmann equation [7] can be written as

$$\frac{\partial f(\mathbf{r},\mathbf{v})}{\partial t} = \int d\mathbf{r}' d\mathbf{v}' L(\mathbf{r},\mathbf{v},\mathbf{r}',\mathbf{v}') \frac{\delta E}{\delta f(\mathbf{r}',\mathbf{v}')} + \frac{\delta \Xi}{\delta \frac{\delta S}{\delta f(\mathbf{r},\mathbf{v})}}, \tag{3.52}$$

where the Poisson bivector field is

$$L(\mathbf{r},\mathbf{v},\mathbf{r}',\mathbf{v}') = \frac{1}{m}\left[\frac{\partial \delta_{\mathbf{v}}}{\partial v'_{\gamma}} \frac{\partial \delta_{\mathbf{r}} f(\mathbf{r}',\mathbf{v}')}{\partial r'_{\gamma}} - \frac{\partial \delta_{\mathbf{r}} f(\mathbf{r},\mathbf{v})}{\partial r_{\gamma}} \frac{\partial \delta_{\mathbf{v}}}{\partial v_{\gamma}}\right], \tag{3.53}$$

where $\delta_{\mathbf{v}} = \delta(\mathbf{v}-\mathbf{v}')$ and $\delta_{\mathbf{r}} = \delta(\mathbf{r}-\mathbf{r}')$. This corresponds to the following Poisson bracket [7]:

$$\begin{aligned}\{A,B\} &= \int d\mathbf{r} \int d\mathbf{v} \int d\mathbf{r}' \int d\mathbf{v}' \frac{\delta A}{\delta f(\mathbf{r},\mathbf{v})} L(\mathbf{r},\mathbf{v},\mathbf{r}',\mathbf{v}') \frac{\delta B}{\delta f(\mathbf{r}',\mathbf{v}')} \\ &= \int d\mathbf{r} \int d\mathbf{v} \frac{f}{m}\left(\frac{\partial A_f}{\partial r_{\gamma}}\frac{\partial B_f}{\partial v_{\gamma}} - \frac{\partial B_f}{\partial r_{\gamma}}\frac{\partial A_f}{\partial v_{\gamma}}\right).\end{aligned} \tag{3.54}$$

The irreversible part of the Boltzmann equation (3.52) is generated by the following dissipation potential [7]:

$$\begin{aligned}\Xi = &\int d1 \int d2 \int d1' \int d2' W(f;1,2,1',2') \\ &\times \left(e^{\frac{X}{2}} + e^{-\frac{X}{2}} - 2\right),\end{aligned} \tag{3.55}$$

where

$$X = \frac{1}{k_B}(S_{f(1)} + S_{f(2)} - S_{f(1')} - S_{f(2')}). \tag{3.56}$$

Numbers 1, 2, 1′, and 2′ denote coordinates $(\mathbf{r}_1,\mathbf{v}_1)$, $(\mathbf{r}_2,\mathbf{v}_2)$, and so on. Energy is specified as

$$E = \int d\mathbf{r} \int d\mathbf{v}\, (1/2mv^2 + m\phi(r)) f(r,v)$$

where $\phi(r)$ is a constant external potential field. Entropy is specified as the standard Boltzmann entropy [7],

$$S = -k_B \int d\mathbf{r} \int d\mathbf{v} f(\mathbf{r},\mathbf{v}) \log f(\mathbf{r},\mathbf{v}), \tag{3.57}$$

which is obviously even with respect to TRT.

TRT applied on probability distribution inverts velocities, i.e.,

$$\mathbf{I} f(\mathbf{r},\mathbf{v}) = f(\mathbf{r},-\mathbf{v}). \tag{3.58}$$

Let us now formulate the notion of reversibility or irreversibility geometrically. The manifold $\mathcal{M}$ is given by probability density at each place of phase space $f(\mathbf{r},\mathbf{v})$. TRT is given by (3.58) and the Jacobi matrix of the transformation is thus given by

$$\begin{aligned}\frac{\partial \mathbf{I}(f(\mathbf{r},\mathbf{v}))}{\partial f(\mathbf{r}',\mathbf{v}')} &= \frac{\partial \int d\mathbf{r} \int d\mathbf{v} \delta(\mathbf{v}+\mathbf{v}')\delta(\mathbf{r}-\mathbf{r}') f(\mathbf{r}',\mathbf{v}')}{\partial f(\mathbf{r}',\mathbf{v}')} \\ &= \delta(\mathbf{r}-\mathbf{r}')\delta(\mathbf{v}+\mathbf{v}').\end{aligned} \tag{3.59}$$

The vector field generating reversible evolution in Boltzmann equation is equal to

$$\mathcal{V} = \int d\mathbf{r} \int d\mathbf{v} \int d\mathbf{r}' \int d\mathbf{v}' L(\mathbf{r},\mathbf{v},\mathbf{r}',\mathbf{v}') \frac{\delta E}{\delta f(\mathbf{r}',\mathbf{v}')} \frac{\partial}{\partial f(\mathbf{r},\mathbf{v})}, \tag{3.60}$$

where $L(\mathbf{r},\mathbf{v},\mathbf{r}',\mathbf{v}')$ is specified by formula (3.53). After some algebra, the push-forward induced by TRT transforms the field to

$$\mathbf{I}_{\star}\mathcal{V} = -\int d\mathbf{r}\int d\mathbf{v}\frac{1}{m}\left[\frac{\partial\delta(\mathbf{v}'-\mathbf{v})}{\partial v'_{\gamma}}\frac{\partial\delta(\mathbf{r}'-\mathbf{r})f(\mathbf{r}',-\mathbf{v}')}{\partial r'_{\gamma}} - \frac{\partial\delta(\mathbf{v}'-\mathbf{v})}{\partial v_{\gamma}}\frac{\partial\delta(\mathbf{r}'-\mathbf{r})f(\mathbf{r},-\mathbf{v})}{\partial r_{\gamma}}\right]\frac{\delta E}{\delta f(\mathbf{r}',-\mathbf{v}')}\frac{\partial}{\partial f(\mathbf{r},-\mathbf{v})}, \tag{3.61}$$

which indeed has only a different sign compared with the original field, and one can conclude that the Poisson bracket indeed generates reversible evolution.

Applying TRT onto the dissipation potential means applying the push-forward $\mathbf{I}_{\star}$ as

$$\mathbf{I}_{\star}\Xi = \Xi(\mathbf{I}(f)) = \Xi(f), \tag{3.62}$$

where the last equality follows from simple substitution $-\mathbf{v} \to \mathbf{v}$, etc., in the expression for $\Xi(\mathbf{I}(f))$. The dissipation potential is thus even with respect to TRT and, according to Lemma 3, it only generates irreversible evolution. In summary, we have shown that the Poisson bracket generates reversible evolution while the dissipation potential generates irreversible evolution.

As well as in the case of the master equation in Sec. III D, in the case of the Boltzmann equation we also can introduce new state variables which already have particular parities. For example, the distribution function $f(\mathbf{r},\mathbf{v})$ is fully characterized by its moments with respect to velocity, and the moments have a clear physical interpretation. The zeroth moment

$$\rho(\mathbf{r}) = m\int f(\mathbf{r},\mathbf{v})d\mathbf{r} \tag{3.63}$$

is just density, which is even under TRT. The first moment,

$$\mathbf{u}(\mathbf{r}) = m\int f(\mathbf{r},\mathbf{v})\mathbf{v}d\mathbf{r}, \tag{3.64}$$

is momentum of the fluid (an odd variable), and higher moments may be constructed. Evolution equations for the moments follow from the Boltzmann equation straightforwardly. In particular, for the two first moments we obtain evolution equations of classical hydrodynamics from Sec. III B, where it already has been shown that Theorem 2 applies. Hence, OCRR appear when parity can be assigned to the state variables.

In summary, Theorem 2 does not apply to the Boltzmann equation directly since distribution function itself has no parity. OCRR can be revealed, however, when considering moments of the distribution function, which already have parities, as state variables instead of the distribution function itself. The assumption that relations (2.25) are valid is fulfilled since the Poisson bivector from Boltzmann equation has already been shown to generate only reversible evolution, see Appendix A for independence of reversibility on change of variables. Theorem 2 then applies to these new variables, and its statement, that variables of the same parity are coupled through the dissipative bracket while variables with opposite parities are coupled through the Poisson bracket near equilibrium, is valid for the Boltzmann equation as well.

Before leaving the example of the Boltzmann kinetic equation we emphasize that we regard this historically earliest example of mesoscopic time evolution that manifestly displays the entropic approach to thermodynamic equilibrium states as a time evolution that motivated the formulation of GENERIC. Indeed, it appears (formulated in terms of the dissipation potential) already in Ref. [39]. We also note that since binary collisions can be regarded as chemical reactions in species labeled by the particle momentum $\mathbf{v}$, the formulation shown above can easily be extended to general chemical kinetics [33,40]. A formulation of the Boltzmann equation in terms of nonsymmetric irreversible brackets has been introduced by Öttinger [41].

IV. DISCUSSION

The Onsager-Casimir reciprocal relations were originally formulated by Onsager [1,2] and Casimir [3]. Later they were derived within quantum mechanics by van Kampen [35], and a very detailed derivation was given by de Groot and Mazur [6]. These reciprocity relations have been typically derived from the microscopic time reversibility and the hypothesis that equilibrium fluctuations and macroscopic state variables close to equilibrium follow the same time evolution. On the other hand, Sharipov [42] showed that for OCRR the microscopic reversibility is necessary and sufficient, while other assumptions, e.g., local equilibrium or hypothesis of fluctuation regression, are not. However, he proposes a different relation for OCRR because in a provided example of the velocity slip problem it is shown that a coupled coefficient neither changes nor maintains its own sign (has no parity). Hence OCRR in their standard form (J_k and X_k being a flux-force pair from linear nonequilibrium thermodynamics)

$$\Lambda_{kn} = \mathcal{P}(X_k)\mathcal{P}(X_n)\Lambda_{nk}, \quad J_k = \sum_n \Lambda_{kn}X_n \tag{4.1}$$

cannot be used. He suggests a generalized version of OCRR that is independent of parity of coefficient,

$$\Lambda^t_{kn} = \Lambda^t_{nk}, \tag{4.2}$$

with superscript t denoting the time-reversed kinetic coefficient. This work was further developed for mixture of gases with similar findings [43]. In this paper, we offer an alternative approach to transform to variables with definite parities and to couple evolution equations instead of fluxes and forces, see Secs. III E and IV B.

Pavelka *et al.* [44] showed that TRT also can be used to introduce partial pressures for nonideal mixtures and that the reciprocal relations can depend on the level of description as physical quantities may have different parities on different levels of description.

Geigenmuller *et al.* [45] studied the influence of the presence of fast macroscopic variables on the validity of OCRR. In their view, OCRR are obtained by comparing two levels of description of the same phenomena. They consider a two-step contraction: from the microscopic level to a relatively large number of already-macroscopic variables (both fast and slow); in the second step of contraction, fast variables are eliminated. OCRR are employed on the first contracted level and when the relaxation matrix after the second contraction is studied, it shows second-order deviations from Onsager-Casimir symmetry in the ratio of time scales. Note that OCRR are relations for coupling of evolution equations as in this work.

Wigner [46] provides a discussion on the range of validity of two groups of derivations (the first employs assumptions on the macroscopic laws of motion, and the second assumes a definite statistical law for the path in phase space) of Onsager's reciprocal relations.

Further, van Kampen [47] also used the TRT and parity to study the time variation of probability as given by a special form of the Fokker-Planck equation and identified reversible and irreversible parts (reversibility was implicitly considered as in our Definition 3 for reversibility based on TRT). Interestingly, he shows that the symmetric part of linearized phenomenological equations (derived from the master equation) is a consequence of properties outside of linear regime, whereas the antisymmetry has no counterpart in the nonlinear case. This resembles our conclusions based on the structure of GENERIC.

Additionally, Muschik [48] defines reverse-motion (rm) parameters that change their signs under reversal of motion. He argues that the reversal of motion does not exist macroscopically, whereas the rm parameter is an existing process. Subsequently, OCRR are derived via studying the entropy production under rm-parameter transformation and hence the phenomenological foundations of OCRR are provided. However, Muschik assumes identification of fluxes and forces from the onset, which may be problematic; see Sec. IV B.

An important result in this paper is the relation of antisymmetric coupling to Poisson brackets. Edwards and Beris say that they consider OCRR for dissipative brackets but likely they consider Onsager reciprocity relations only (and which indeed appear through dissipative brackets). OCRR within CIT have also been formulated by Öttinger [15] in terms of so-called bare and dressed symmetries, where relation (2.25b) was derived by use of Green-Kubo's formula. However, the role of Poisson brackets in OCRR was not recognized.

Further, an interesting insight into OCRR has been brought by Mario Liu [49]. His ideas that the behavior of entropy production with respect to TRT should provide OCRR are similar to ideas presented in this paper although presented for the evolution of two state variables only. The results can be extended to an infinite number of variables by mathematical induction straightforwardly. However, the role of Poisson brackets has not been recognized.

A. Nonlinear generalizations

All of the above derivations and treatments of OCRR share that they are only valid near equilibrium although they usually are applied in local equilibrium, which does not need to be near the global equilibrium. Additionally, OCRR are applied in continuum thermodynamics although usually derived only for scalar state variables explicitly. Hence there has been effort to identify an appropriate generalization of OCRR into a nonlinear regime.

Hurley and Garrod [50] used a statistical-mechanics consideration to obtain conditions on a correlation matrix of macroscopic observables. Then, under the assumption of a general linear evolution around an equilibrium and when the dynamics of a point in microscopic phase space is time invariant, a generalization of the OCRR is obtained. If the matrix of the linear evolution is constant, then the standard OCRR are acquired. However, they used a microcanonical ensemble in their derivation that restricts the validity to close proximity of equilibrium similarly to Onsager's regression hypothesis.

Further, Verhás [51] proposed a generalization via a straightforward approach using Taylor's expansion and an assumption on continuity of constitutive relations, $\partial J_i/\partial X_j = \partial J_j/\partial X_k$. Similarly, Astumian [52] considered a higher-order relations among thermodynamic forces and fluxes when analyzing coupled transport, suggesting a generalization of Onsager linear reciprocal relations beyond linear regime. Finally, Ciancio and Verhás showed that some of the nonlinear generalizations of the OCRR are not of general validity as they are not compatible with the law of mass action [53]. The here-proposed approach is compatible with the Guldberg-Waage equations as they have been already formulated within GENERIC [10,40] with an even dissipation potential.

Related work to this manuscript can be identified in the work [54] of Miroslav Grmela in 2002. He also studied OCRR and provided an extension to contact geometry formulation of GENERIC. Further, he also introduced TRT and parity (using projector operators), and coupling was not considered among forces and fluxes but rather among evolution equations. In addition, the thermodynamic potential Φ and energy E were taken as invariant with respect to TRT (even functionals). In our current study, we are focusing on a careful discussion of (ir)reversibility in its various forms and reveal the implications of OCRR on structure of evolution equations including GENERIC. In particular, we show that antisymmetric coupling is exclusively mediated by Poisson bracket and symmetric coupling by dissipation potentials or brackets. Further, we shed light on some problems related to OCRR within classical linear irreversible thermodynamics; see Sec. IV B.

B. Problems related to OCRR and relevance of this work

Apart from some controversies mentioned above, we shall elaborate on one related to the appropriate choice of fluxes and forces for OCRR. Coleman and Truesdell provide a careful discussion of implications of OCRR on flux-force relations [55]. They argue that if entropy production is considered as bilinear and, in addition, linear flux-force relations are taken into account, one cannot employ OCRR. The reason is that regular linear transformation (where fluxes and forces are combined together) can lead to losing (anti)symmetry in the force-flux relations. Hence, it is required to have some independent identification of relevant fluxes and forces in order to employ OCRR and closures as a result. Additionally, Meixner showed that if forces and fluxes exist such that satisfy linear flux-force relations and form the bilinear form of entropy production, then, in fact, infinitely many choices of fluxes and forces are possible that have the same properties and, moreover, satisfy the symmetry condition of the linear phenomenological matrix [6,56,57]. Andrews [58] comes to a similar conclusion and suggests that no amount of macroscopic analysis can yield the reciprocal relations. Note that he was aware that the antisymmetric part does not produce entropy and, hence, in a sense, corresponds to reversible processes (including the example of the coupling between rate of a chemical reaction and the divergence of the local velocity).

In summary, the problem with selection of thermodynamic fluxes and forces results in uncertainty of applicability of OCRR in particular cases. In this paper OCRR are regarded as a consequence of the structure of the GENERIC framework. If this structure is not recognized, OCRR are usually applied to force-flux relations inferred from a formula for entropy production [6]. This brings up the question of how thermodynamic fluxes and forces should be identified. In this approach of classical irreversible thermodynamics, independent (experimental or microscopic) insight is thus required for symmetry or antisymmetry of phenomenological matrix. If, on the other hand, OCRR are implied by the structure of GENERIC as in this paper, the question regarding how to identify the forces and fluxes is irrelevant since the structure of GENERIC is invariant to the transformation of state variables [15].

Now we are ready to state the relevance of this paper to OCRR and the related problems as described above. This text unifies various notions of (ir)reversibility, addresses the problem of flux-force identification, offers a plausible nonlinear extension of OCRR valid in wide range on scenarios, and assesses implications of OCRR on the structure of evolution equations (GENERIC), including coupling phenomena.

V. CONCLUSION

The abstract GENERIC equation (2.11) collects some of the features that are emerging in mesoscopic dynamics of macroscopic systems (as, for instance, the time irreversibility and dissipativity). In order to see their meaning and their significance, we can attempt to relate them either to certain features of the microscopic dynamics or, alternatively, to thermodynamics and macroscopic multiscale dynamics. In this paper we do the latter. Our objective has been in particular to explore the interrelationships among the time irreversibility, the dissipativity, and the thermodynamics. The connection with thermodynamics has also been explored by Grmela [54], and, more recently [9], GENERIC has been lifted into a larger space in which the time evolution appears to be a continuous sequence of contact-structure preserving transformations extending in a direct way, with the Legendre transformations playing an important role in the classical thermodynamics.

As for making contacts with the microscopic dynamics, we recall in particular the work of Onsager [1,2] and Casimir [3]. In the Onsager's analysis, the Onsager symmetry of the linearized mesoscopic dynamics arises from an assumption about the microscopic dynamics, namely from the assumption that microscopic fluctuations of mesoscopic state variables follow, in states that are not far from the thermodynamic equilibrium, the mesoscopic time evolution. Various aspects of Onsager's work have been then explored and further developed, see Sec. IV.

We note that not all of the extensions of the Onsager's work that have been attempted and that can be found in the literature lead to dynamical systems that are particular realizations of the abstract GENERIC equation [7,8]. As we have already mentioned in Sec. II F, GENERIC (2.11) does not intend to be all inclusive. Our principal objective has been to formulate a mesoscopic dynamics that has the following features:

(a) the formulation is sufficiently abstract so it is usable on any mesoscopic level of description,

(b) the dynamics has a rich structure with many clearly verifiable consequences,

(c) the dynamics is inclusive in the sense that the mesoscopic dynamical systems that have arisen in attempts to record and understand results of mesoscopic experimental observations are either particular realizations of Eq. (2.11) or certain reductions of the equation (see Sec. II F), and

(d) the dynamics has the thermodynamic interpretation in the sense that it describes the approach to a more macroscopic level of description.

In Sec. II A we introduce the concept of TRT, which is specified rigorously in Sec. II E. Reversible evolution is identified as the part of evolution which is not altered by TRT while irreversible evolution changes its sign after applying TRT, see Definition 3. This concept of reversibility based on TRT is equivalent to entropic definition of reversibility, Definition 4, where irreversible evolution is identified as the part of evolution which raises entropy. Yet another definition comes from GENERIC where reversible evolution is identified as the evolution generated by a Poisson bracket while irreversible evolution is generated by a dissipation potential or dissipative bracket, see Definition 5. While it can be shown that, under certain assumptions, all of these definitions of irreversible evolution coincide, see Sec. II E, it is not clear how to prove the analogical statement for the reversible evolution. To our best knowledge this is an open problem although it is quite likely that the definitions coincide as well as for the irreversible evolution since we are not aware of any counterexample and since it is supported by projection operator arguments, see Sec. II E.

After introducing TRT properly, OCRR are shown to be implied by the structure of GENERIC in the near-equilibrium regime without limitations to finite-dimensional dynamics or continuum thermodynamics. The symmetric part of the relations is given by the dissipative bracket (or dissipation potential) while the antisymmetric is given by the Poisson bracket. This way, OCRR can be regarded as a near-equilibrium consequence of the structure of GENERIC. In this sense, OCRR are generalized into the far-from-equilibrium regime since the far-from-equilibrium structure which implies them is identified.

In addition, we shed light on the following problem related to OCRR within classical linear irreversible thermodynamics. OCRR in the classical sense require an independent identification of thermodynamic fluxes and forces first, as linear transformation may result in a change of structure (symmetricity) of phenomenological coefficients. Hence the knowledge of entropy production and linear flux-force constitutive relations is not enough to utilize OCRR. In contrast, our approach couples directly the evolution equations of the system at hand by the means of identification of the GENERIC structure and, due to its invariance to transformation of variables, the problem of coupling fluxes and forces disappears. GENERIC with dissipation potential is thus a natural framework for OCRR that is valid far from equilibrium and lacks the flux-force identification problem.

Finally, both TRT and the generalized OCRR are illustrated in Hamiltonian dynamics, classical hydrodynamics, the classical theory of mixtures, the quantum master equation, and the Boltzmann equation.

ACKNOWLEDGMENTS

We are grateful to František Maršík for his generous support and for revealing the world of thermodynamics to M.P. and V.K. The work was developed within the POLYMEM project, Reg. No CZ.1.07/2.3.00/20.0107, which is cofunded from the European Social Fund (ESF) in the Czech Republic ("Education for Competitiveness Operational Programme") and within the CENTEM project, Reg. No. CZ.1.05/2.1.00/03.0088, cofunded by the ERDF as part of the Ministry of Education, Youth and Sports OP RDI programme. This project was partially supported by Natural Sciences and Engineering Research Council of Canada (NSERC).

APPENDIX A: FURTHER GEOMETRICAL PROPERTIES

Is definition of reversibility (2.36) independent of the particular choice of variables (keeping the level of description)? Suppose that there is a diffeomorphism ϕ converting coordinates $\mathbf{x}$ into $\mathbf{x}'$, i.e.,

$$x' = \phi(\mathbf{x}), \tag{A1}$$

and that relation (2.36) holds true for the evolution. TRT acts on $\mathbf{x}'$ as $\mathbf{I}'$ defined by

$$\mathbf{I}' = \phi \circ \mathbf{I} \circ \phi^{-1}. \tag{A2}$$

Evolution of the new variables is clearly given by

$$\frac{dx'^i}{dt} = \frac{\partial x'^i}{\partial x^j} V^j \Big|_{\phi^{-1}(\mathbf{x}')} . \tag{A3}$$

Evolution of inverted variables then becomes

$$\begin{aligned}\frac{d\mathbf{I}'^i(\mathbf{x}')}{dt} &= \frac{\partial \mathbf{I}'^i}{\partial x'^j}\frac{\partial x'^j}{\partial x^k} V^k \Big|_{\phi^{-1}(\mathbf{x}')}\\ &= \frac{\partial x'^i}{\partial x^l}\frac{\partial \mathbf{I}^l}{\partial x^m}\underbrace{\frac{\partial x^m}{\partial x'^j}\frac{\partial x'^j}{\partial x^k}}_{\delta^m_k} V^k \Bigg|_{\phi^{-1}(\mathbf{x}')}\\ &= \frac{\partial x'^i}{\partial x^l}\frac{\partial \mathbf{I}^l}{\partial x^k} V^k \Big|_{\phi^{-1}(\mathbf{x}')} = -\frac{\partial x'^i}{\partial x^l} V^l \Big|_{\mathbf{I}\circ\phi^{-1}(\mathbf{x}')}\\ &= -\frac{\partial x'^i}{\partial x^l} V^l \Big|_{\phi^{-1}(\mathbf{I}'(\mathbf{x}'))},\end{aligned} \tag{A4}$$

which only differs in sign from (A3) and thus generates only reversible evolution according to Definition 6. The minus sign has appeared due to usage of relation (2.36). If, on the other hand, the vector field were irreversible, i.e., relation (2.41) would be used instead of (2.36), the minus sign would not appear and the resulting right-hand side would generate irreversible evolution according to Definition 7. Therefore, the following theorem has been proven:

Theorem 3 (independence on choice of variables). Definitions of reversibility and irreversibility (6 and 7) are independent of the choice of variables. In other words, after a change of variables (by a diffeomorphism) the new Poisson bracket still generates the reversible evolution while the new dissipation potential (or dissipative bracket) still generates the irreversible evolution.

This is also what one would expect since relations (2.36) and (2.41) are written in a form invariant to coordinate transformations.

Consequently, if a Poisson bracket is reversible, all Poisson brackets obtained by simple change of variables (diffeomorphism) are reversible. In particular, on the level of Hamiltonian dynamics, where the canonical Poisson bracket is of course reversible as has been demonstrated in Sec. III A, any Poisson bracket is reversible. Indeed, because it expresses the same evolution as the canonical bracket, it has to be possible to obtain it from the canonical bracket by change of variables. We have thus come to the following lemma:

Lemma 4. Any Poisson bracket on the level of Hamiltonian dynamics generates only reversible evolution, i.e., it fulfills relation (2.36).

APPENDIX B: TIME EVOLUTION NEAR EQUILIBRIUM

An interesting question arises: What can one say about the spectrum of the linear operator satisfying the Onsager-Casimir symmetry? In other words, what are consequences of the Onsager-Casimir relations on the solutions of the linear equation, i.e., on the evolution to the equilibrium?

In the particular case, when the state space is finite dimensional and the time-reversal transformation $\mathbf{I}$ is identity, i.e., only even state variables are present, the linear operator governing the linearized time evolution, $\mathbf{M}(x_{\text{th}})$, is symmetric and positive definite. It is well known in linear algebra that such an operator can be diagonalized, its eigenvalues are all real and positive, and eigenspaces are orthogonal. As a result, in an appropriate coordinate system (given by eigenvectors), the time evolution is actually an uncoupled relaxation to the thermodynamic equilibrium.

Let us now consider the case when all state variables have parity (see Sec. III D for how to tackle a situation when state variables do not posses any parity) and the state space is finite dimensional. The linearized system is (2.28) with the matrix $\mathbf{K}$ of the linearized system,

$$K_{ij} = T L_{ij}(x_{\text{th}}) - M_{ij}(x_{\text{th}}),$$

consisting of both antisymmetric $T\mathbf{L}(x_{\text{th}})$ and symmetric part $\mathbf{M}(x_{\text{th}})$.

Having the operator $\mathbf{I}$, it is now natural to introduce an indefinite inner product $\langle \bullet, \mathbf{I}\bullet \rangle$. OCRR are then equivalent to symmetry with respect to this product, and some spectral consequences can be revealed; see Appendix C.

First, note that any matrix can be decomposed into its antisymmetric and symmetric parts and that this decomposition is unique, i.e., $T\mathbf{L}(x_{\text{th}})$ and $-\mathbf{M}(x_{\text{th}})$ is such a unique decomposition of the linearized governing equations of time-evolution equations, the matrix $\mathbf{K}$. Next, we shall show that there is a relation between a spectrum of a matrix and its symmetric part.

Lemma 5. Let $\mathbf{A} \in R^{n,n}$ be a n-dimensional real matrix and $\mathbf{S} = 1/2\left(\mathbf{A} + \mathbf{A}^T\right)$ its symmetric part. Then, for the spectrum of these matrices, it holds that $\Re(\sigma(\mathbf{A})) \subset \sigma(\mathbf{S})$.

Proof. Let $\lambda \in \sigma(\mathbf{A})$, and thus $\lambda x = \mathbf{A}x$ and $\|x\| = 1 = \langle x^*, x\rangle$, where * denotes complex conjugate($\overline{x}$) and transposition (x^T). Note that all eigenvectors for complex eigenvalues are complex as can be seen by a contradiction from $\lambda x = \mathbf{A}x$.

Hence we have $\lambda = x^*\mathbf{A}x$, $\lambda = x^T\mathbf{A}^T\overline{x}$, $\overline{\lambda} = x^T\mathbf{A}\overline{x}$. As a result,

$$\Re(\lambda) = 1/2(\lambda + \overline{\lambda}) = 1/2(x^T\mathbf{A}\overline{x} + x^T\mathbf{A}^T\overline{x})$$
$$= x^*(1/2(\mathbf{A} + \mathbf{A}^T))x = x^*\mathbf{S}x,$$

which concludes the proof as $x^*\mathbf{S}x \subset \sigma(\mathbf{S})$.

Corollary 2. The identified Onsager-Casimir relations with state variables with either parity guarantee relaxation to the thermodynamic equilibrium, as the real part of the spectrum of the linearized system is a subset of the minus (note the minus sign in the $\mathbf{K}$ matrix) spectrum of the linearized operator of the dissipation dynamics which is symmetric and positive definite.

APPENDIX C: INDEFINITE INNER PRODUCT

In this section we show that a matrix $\mathbf{K}$ satisfies OCRR if and only if it is symmetric with respect to the following indefinite inner product:

$$\langle \bullet, \mathbf{I}\bullet \rangle. \tag{C1}$$

Symmetry with respect to this product means that

$$\langle \mathbf{Kx}, \mathbf{Iy} \rangle = \langle \mathbf{x}, \mathbf{IKy} \rangle \quad \forall \mathbf{x}, \mathbf{y} \tag{C2}$$

or, in terms of components,

$$K_{ij}(x_j\mathbf{I}(y_i) - x_i\mathbf{I}(y_j)) = 0 \quad \forall x_i, x_j, y_i, y_j. \tag{C3}$$

Equation (C3) for all the following cases: (i-even, j-even), (i-even, j-odd), (i-odd, j-even), (i-odd, j-odd) gives that

$$(K_{ij} - K_{ji})x_j y_i = 0 \quad \text{for } i \text{ and } j \text{ with the same parities,} \tag{C4}$$

$$(K_{ij} + K_{ji})x_j y_i = 0 \quad \text{for } i \text{ and } j \text{ with the opposite parities.} \tag{C5}$$

In other words, the antisymmetric part of matrix $\mathbf{K}$ couples variables with opposite parities while the symmetric part couples variables with the same parities, which is exactly the statement that the matrix satisfies OCRR. We have thus proven the following lemma:

Lemma 6. A matrix satisfies OCRR if and only if it is symmetric with respect to indefinite inner product $\langle \bullet, \mathbf{I}\bullet \rangle$.

Having shown that the matrix $\mathbf{K}$, which generates evolution in the sense of linearized GENERIC, is symmetric with respect to the indefinite scalar product constructed from TRT, many mathematical properties of the evolution equations are immediately revealed [59]. In particular, Grmela and Iscoe [60] proved existence, uniqueness, and boundedness for initial value problems as well as that evolution operators form a strongly continuous semigroup of contractions and that the linearized evolution equations are diagonalizable in the finite-dimensional case. Moreover, Grmela *et al.* [61] showed the consequences of the symmetry on the spectrum of the $\mathbf{K}$ matrix. In summary, it is quite useful to realize that OCRR imply symmetry of the matrix-generating near-equilibrium evolution with respect to indefinite scalar product (C1) and, consequently, many mathematical properties of the near-equilibrium evolution equations can be derived.

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[1] L. Onsager, Phys. Rev. **37**, 405 (1931).
[2] L. Onsager, Phys. Rev. **38**, 2265 (1931).
[3] H. B. G. Casimir, Rev. Mod. Phys. **17**, 343 (1945).
[4] C. Maes and K. Netočný, J. Stat. Phys. **110**, 269 (2003).
[5] For a quantum-mechanical interpretation, see Sec. III D.
[6] L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part 1*, 3rd ed. (Elsevier, Amsterdam, 2013), Vol. 5.
[7] M. Grmela and H. C. Öttinger, Phys. Rev. E **56**, 6620 (1997).
[8] H. C. Öttinger and M. Grmela, Phys. Rev. E **56**, 6633 (1997).
[9] M. Grmela, Entropy **16**, 1652 (2014).
[10] M. Grmela, Adv. Chem. Eng. **39**, 75 (2010).
[11] J. Waldram, *The Theory of Thermodynamics* (Cambridge University Press, Cambridge, 1985).
[12] D. Jou, J. Casas-Vázquez, and G. Lebon, *Extended Irreversible Thermodynamics*, 4th ed. (Springer-Verlag, New York, 2010).
[13] M. Hütter and B. Svendsen, Continuum Mech. Thermodynam. **25**, 803 (2013).
[14] M. Fecko, *Differential Geometry and Lie Groups for Physicists* (Cambridge University Press, Cambridge, 2006).
[15] H. Öttinger, *Beyond Equilibrium Thermodynamics* (Wiley, New York, 2005).
[16] C. Villani, Phys. Plasmas **21**, 030901 (2014).
[17] A. Vlasov, Sov. Phys. Usp. **10**, 721 (1968).
[18] L. Landau, Zhurn. Eksperiment. Teoret. Fiz. **16**, 574 (1946).
[19] H. C. Öttinger, Phys. Rev. E **90**, 042121 (2014).
[20] J. Marsden, T. Ratiu, and A. Weinstein, Transact. Am. Math. Soc. **281**, 147 (1984).
[21] M. Grmela, J. Non-Newtonian Fluid Mech. **165**, 980 (2010).
[22] J. F. Gu and M. Grmela, J. Non-Newtonian Fluid Mech. **152**, 12 (2008).
[23] M. Grmela, G. Maitrejean, F. Chinesta, and A. Ammar, Rheol. Acta **52**, 557 (2013).
[24] H. Poincaré, D. Goroff, and D. Goroff, *New Methods of Celestial Mechanics*, History of Modern Physics and Astronomy (American Institute of Physics, New York, 1997).
[25] For compactness of notation, time dependence of state variables is not written explicitly.
[26] Gradient of δ distribution $\frac{\partial \delta}{\partial \mathbf{r}'}$ can be expressed as $\frac{\partial \delta_{\mathbf{r}}(\mathbf{r}')}{\partial \mathbf{r}'}$ more rigorously. We also suppose that all functions are sufficiently regular so all mathematical expressions are well defined.
[27] H. C. Öttinger, J. Chem. Phys. **130**, 114904 (2009).
[28] L. Landau, E. Lifshitz, and L. Pitaevskii, *Statistical Physics*, Course of Theoretical Physics Part 2 (Butterworth-Heinemann, London, 1980).

[29] H. Callen, *Thermodynamics: An Introduction to the Physical Theories of Equilibrium Thermostatics and Irreversible Thermodynamics* (Wiley, New York, 1960).
[30] Note that the original Poisson bracket satisfies the condition and, consequently, if a new term should be added, the term has to satisfy the condition itself as well.
[31] V. Klika and F. Maršík, J. Phys. Chem. B **113**, 14689 (2009).
[32] V. Klika, J. Phys. Chem. B **114**, 10567 (2010).
[33] V. Klika and M. Grmela, Phys. Rev. E **87**, 012141 (2013).
[34] V. Klika and M. Grmela, J. Chem. Phys. **140**, 124110 (2014).
[35] N. V. Kampen, Physica **20**, 603 (1954).
[36] L. Landau and E. Lifshitz, *Quantum Mechanics: Non-relativistic Theory* (Butterworth-Heinemann, London, 1977).
[37] A. Das, *Lectures on Quantum Field Theory* (World Scientific, Singapore, 2008).
[38] Check the proof to see that the meaning can indeed be inverted in this way.
[39] M. Grmela, Contemp. Math. **28**, 125 (1984).
[40] M. Grmela, Physica D Nonlinear Phenomena **241**, 976 (2012).
[41] H. Ottinger, J. Non-Equil. Thermodynam. **22**, 386 (1997).
[42] F. Sharipov, Phys. Rev. E **73**, 026110 (2006).
[43] F. Sharipov and D. Kalempa, J. Stat. Phys. **125**, 661 (2006).
[44] M. Pavelka, F. Maršík, and V. Klika, Int. J. Eng. Sci. **78**, 192 (2014).
[45] U. Geigenmüller, U. Titulaer, and B. Felderhof, Physica A: Stat. Mech. Appl. **119**, 53 (1983).
[46] E. P. Wigner, J. Chem. Phys. **22**, 1912 (1954).
[47] N. Van Kampen, Physica **23**, 816 (1957).
[48] W. Muschik, Period. Polytech.-Chem. **42**, 85 (1998).
[49] M. Liu, arXiv:cond-mat/9806318.
[50] J. Hurley and C. Garrod, Phys. Rev. Lett. **48**, 1575 (1982).
[51] J. Verhas, Ann. Phys. **495**, 189 (1983).
[52] R. D. Astumian, Phys. Rev. Lett. **101**, 046802 (2008).
[53] V. Ciancio and J. Verhás, J. Non-Equil. Thermodynam. **19**, 184 (1994).
[54] M. Grmela, Physica A: Stat. Mech. Appl. **309**, 304 (2002).
[55] B. D. Coleman and C. Truesdell, J. Chem. Phys. **33**, 28 (1960).
[56] J. Meixner, Ann. Phys. **435**, 244 (1943).
[57] J. Meixner, Adv. Molecular Relax. Process. **5**, 319 (1973).
[58] F. Andrews, Indust. Eng. Chem. Fundam. **6**, 48 (1967).
[59] J. Bognár, *Indefinite Inner Product Spaces*, Ergebnisse der Mathematik und ihrer Grenzgebiete (Springer, Berlin, 1974).
[60] M. Grmela and I. Iscoe, Ann. Inst. Henry Poincaré **28**, 111 (1978).
[61] M. Grmela, R. Rosen, and L. Garcia-Colin, J. Chem. Phys. **75**, 5474 (1981).