Preservation of thermodynamic structure in model reduction

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Based on the availability of an invariant manifold, we develop a model-reduction procedure that preserves thermodynamic structure. More concretely, we construct the Poisson and irreversible brackets of the general equation for the nonequilibrium reversible-irreversible coupling of nonequilibrium thermodynamics by means of the ideas originally introduced for handling constraints. The general ideas are then applied to the Kramers problem, that is, the description of transitions between two potential wells separated by a high barrier. This example reveals how a fortuitous cancellation mechanism that allows a logarithmic entropy to generate a linear diffusion equation is inherited by a master equation resulting from model reduction.

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I. INTRODUCTION

Model reduction is an important way of simplifying dynamic systems. An overview of the variety of applications and different reduction methods for linear and nonlinear dynamic systems can be found in the reviews [1–5]. We here address the question whether the property of being thermodynamically admissible is preserved in a typical model-reduction procedure. Of course, we first need to clarify the precise meaning of the phrases in quotation marks.

We here use the definition that a set of evolution equations is thermodynamically admissible if it possesses the structure of the general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) [6–8]. In that approach, the reversible contribution to time evolution is assumed to be of Hamiltonian form and hence requires an energy function and a Poisson bracket, which reflects the idea that the reversible time evolution should be under mechanistic control. The remaining irreversible contribution is generated by the nonequilibrium entropy by means of an irreversible bracket. A brief summary of the GENERIC framework of nonequilibrium thermodynamics is offered in Sec. II. An overview of the development of the general field of nonequilibrium thermodynamics since 1996, also showing the role of the GENERIC approach within this field, can be obtained from the proceedings of a series of international workshops on the topic and the corresponding workshop reports [9–14].

For model reduction, we rely on the idea of inertial or invariant manifolds (see, e.g., [2,5,15,16]). If we start the evolution on an invariant manifold imbedded in a larger space, the trajectory stays rigorously or, at least, approximately on the manifold. Our task is to identify the GENERIC structure for the evolution equations formulated intrinsically in the manifold, provided that the original equations in the large space possess GENERIC structure. This is the task we take on in Sec. III. For the proposed construction, it is irrelevant whether the invariant manifold is rigorous or approximate. For our analysis of thermodynamic admissibility we assume that the invariant manifold be given whereas, in general, finding the invariant manifold is the most important goal of model reduction.

For completing our task we heavily rely on the methods for treating dynamic systems with constraints. The proper treatment of Hamiltonian systems with constraints was developed by Dirac in the context of gauge conditions for gravity [17,18]. His construction of a Poisson bracket on a constrained manifold can easily be adapted to irreversible brackets [19]. The problems of constraints and model reduction are intimately related as we need to constrain a thermodynamically admissible evolution equation from a large space to an invariant manifold in both cases. However, there are some differences in the details. In dealing with constraints, one usually eliminates only a small fraction of the degrees of freedom and one often formulates evolution equations in the original large space. In model reduction, one often eliminates almost all degrees of freedom and one looks for equations formulated intrinsically in the low-dimensional manifold of the remaining degrees of freedom.

For the example of diffusion in a symmetric double-well potential with a high potential barrier between the wells, which is discussed in great detail in Sec. IV, we reduce from an infinite-dimensional space of probability densities to an approximately invariant one-dimensional manifold. From this example we learn how a seemingly artificial feature of the irreversible bracket arises in a perfectly natural way.

II. THERMODYNAMIC FRAMEWORK

Our summary of the GENERIC formulation of time-evolution for nonequilibrium systems [6–8] is based on Ref. [19]. If A is an arbitrary observable, that is, a sufficiently regular real-valued function or functional of a set of variables x required for a complete description of a given nonequilibrium system, the time evolution of A is given by

$$\frac{dA}{dt} = \{A,E\} + [A,S]. \tag{1}$$

The observables E and S generating time evolution are the total energy and entropy of the system, and $\{\cdot,\cdot\}$ and $[\cdot,\cdot]$ are the Poisson and irreversible brackets, respectively. The two contributions to the time evolution of A generated by the total energy E and the entropy S in Eq. (1) are the reversible and irreversible contributions, respectively. Equation (1) is supplemented by the complementary degeneracy requirements

$$\{S,A\} = 0, \quad [E,A] = 0, \tag{2}$$

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which hold for all observables A. The requirement that the entropy is a degenerate functional of the Poisson bracket underlines the reversible nature of the Hamiltonian contribution to the dynamics. The requirement that the energy is a degenerate functional of the irreversible bracket expresses the conservation of the total energy in a closed system, even when energy is dissipated.

For completeness, we summarize some important properties of Poisson and irreversible brackets. The Poisson bracket is antisymmetric and satisfies the Jacobi identity

$$\{A,\{B,C\}\} + \{B,\{C,A\}\} + \{C,\{A,B\}\} = 0, \tag{3}$$

for arbitrary observables A, B, and C. These properties are well known from the Poisson brackets of classical mechanics, and they express the essence of reversible dynamics. The irreversible bracket is symmetric (for a more sophisticated discussion of the Onsager-Casimir symmetry properties of the irreversible bracket, see Secs. 3.2.1 and 7.2.4 of Ref. [8] as well as Ref. [20]) and satisfies the non-negativeness condition

$$[A,A] \geqslant 0. \tag{4}$$

This non-negativeness condition, together with the proper degeneracy requirement, guarantees that the entropy is a nondecreasing function of time or, in other words, the second law of thermodynamics,

$$\frac{dS}{dt} = [S,S] \geqslant 0. \tag{5}$$

Only the second term in Eq. (1) determines the entropy production, which demonstrates its irreversible character.

In practical calculations, it is often convenient to formulate GENERIC in terms of Poisson and friction operators instead of brackets [7,8]. More precisely, one writes

$$\{A,B\} = \frac{\delta A}{\delta x} L \frac{\delta B}{\delta x}, \tag{6}$$

and

$$[A,B] = \frac{\delta A}{\delta x} M \frac{\delta B}{\delta x}, \tag{7}$$

where L is the Poisson operator and M is the friction operator. The time-evolution equations for the system variables x implied by Eq. (1) can then be expressed in the form

$$\frac{dx}{dt} = L\frac{\delta E}{\delta x} + M\frac{\delta S}{\delta x}. \tag{8}$$

III. THERMODYNAMIC MODEL REDUCTION

We now proceed to construct a thermodynamically admissible evolution equation on a submanifold of a given thermodynamic system. We rely on the ideas developed in Ref. [19] for the thermodynamically consistent treatment of constraints. For model reduction, the submanifold defined by the constraints is to be taken as the invariant manifold assumed to be available.

Whereas observables can easily be restricted to the manifold, the key problem is to define valid Poisson and irreversible brackets on the manifold. If a submanifold of the large space is given by the functions $x(y)$ in terms of the intrinsic coordinates y, we define $\bar{A}(y) = A(x(y))$ for every observable A on the large space. For the gradient of the observable $\bar{A}$ in the manifold we then have the chain rule

$$\frac{\delta \bar{A}}{\delta y} = \frac{\delta A}{\delta x}\frac{\partial x}{\partial y}, \tag{9}$$

introducing the tangential components of the gradient in the large space.

To make contact to previous work, we assume that the manifold is alternatively characterized by holonomic constraints of the form

$$\Pi_\alpha(x) = 0, \tag{10}$$

where the label α can be discrete or continuous. If the constraints are independent, the coordinates (y,Π) are in a one-to-one relationship to the coordinates x of the large space (at least, locally).

A. Poisson bracket

For the proper treatment of gauge conditions in the quantization of gauge field theories, Dirac [17,18] developed a constrained Poisson bracket. For a finite number of constraint conditions, his famous bracket can be written as (see, for example, Sec. 8.5 of Ref. [21], ch. 1 of Ref. [22], and references therein)

$$\{A,B\}^{\mathrm{c}} = \{A,B\} - \sum_{\alpha\beta}\{A,\Pi_\alpha\}J^{\mathrm{p}}_{\alpha\beta}\{\Pi_\beta,B\}, \tag{11}$$

where $J^{\mathrm{p}}_{\alpha\beta}$ is the inverse of the matrix $\{\Pi_\alpha,\Pi_\beta\}$. As we wish to evaluate $\{A,B\}^{\mathrm{c}}$ on the manifold, also the matrix $J^{\mathrm{p}}_{\alpha\beta}$ needs to be calculated on the manifold only. In operator notation, Eq. (11) can be written as

$$\{A,B\}^{\mathrm{c}} = \frac{\delta A}{\delta x}(L - LR^{\mathrm{p}}L)\frac{\delta B}{\delta x}, \tag{12}$$

where

$$R^{\mathrm{p}}_{jk} = \sum_{\alpha\beta}\frac{\delta\Pi_\alpha}{\delta x_j}J^{\mathrm{p}}_{\alpha\beta}\frac{\delta\Pi_\beta}{\delta x_k}. \tag{13}$$

Note that the matrices J^{p} and R^{p} depend on the original Poisson operator L and on the invariant manifold, but not on the observable A. When the constrained bracket is evaluated on the manifold, the gradients of the observables A and B on the right-hand side of Eq. (12) may be replaced by their tangential components. This remark follows from the observation

$$R^{\mathrm{p}}L\frac{\delta\Pi}{\delta x} = \left(\frac{\delta\Pi}{\delta x}J^{\mathrm{p}}\frac{\delta\Pi}{\delta x}\right)L\frac{\delta\Pi}{\delta x} = \frac{\delta\Pi}{\delta x}, \tag{14}$$

which is based on the definitions of R^{p} and J^{p}. Note that this identity implies that $R^{\mathrm{p}}L$ and LR^{p} are projectors.

The existence of the inverse of the matrix $\{\Pi_\alpha,\Pi_\beta\}$ is nontrivial. In choosing the constraints Π_α, one should clearly avoid degenerate functions, such as the entropy in Eq. (2), which are conserved quantities of the reversible dynamics. The construction of constrained brackets should be performed within the submanifold characterized by constant values of the degenerate functions (that is, within symplectic leaves). Even then, a set of independent constraints needs to be chosen carefully for the matrix $\{\Pi_\alpha,\Pi_\beta\}$ to be invertible on the

invariant manifold. In the nomenclature of Dirac [17], the Π_α have to form a set of second-class constraints, that is, each constraint has to have a nonzero Poisson bracket with at least one other constraint.

For the generalization of Dirac's bracket to an infinite number of constraints, the constrained Poisson bracket can alternatively be constructed by considering a modified observable

$$A^{\mathrm{p}}(x) = A(x) + \sum_\alpha \lambda_\alpha^A(x)\Pi_\alpha(x), \tag{15}$$

for every observable A. If α is a continuous label, the sum is to be replaced by an integral. The Lagrange multipliers $\lambda_\alpha^A(x)$ are to be chosen such that

$$\frac{\delta\Pi_\alpha}{\delta x} L \frac{\delta A^{\mathrm{p}}}{\delta x} = \{\Pi_\alpha, A^{\mathrm{p}}\} = 0, \tag{16}$$

for all α as an identity on the manifold, but otherwise arbitrary. The observables Π_α and A^{p} are defined on the large space, and so is the observable $\{\Pi_\alpha, A^{\mathrm{p}}\}$. The size of the linear problem to be solved (matrix inversion to obtain $J^{\mathrm{p}}_{\alpha\beta}$ or linear system for λ_α^A) is given by the number of constraints. On the manifold, Eq. (10) implies that the modified observable A^{p} defined in Eq. (15) coincides with A. In general, the Lagrange multipliers λ_α^A are not unique, nor is there a guarantee for the existence of a solution to the system of linear equations in Eq. (16). The constraints Π_α should be chosen as described above. If suitably modified observables A^{p} can be constructed, as needs to be verified for the chosen constraints, the constrained Dirac bracket is given by

$$\{A,B\}^{\mathrm{c}} = \{A^{\mathrm{p}}, B^{\mathrm{p}}\} = \frac{\delta A^{\mathrm{p}}}{\delta x} L \frac{\delta B^{\mathrm{p}}}{\delta x}. \tag{17}$$

On the manifold, $\{A,B\}^{\mathrm{c}}$ is independent of the modifications A^{p} and B^{p} of the form (15), that is, independent of the choice of the Lagrange multipliers, as long as the conditions (16) are satisfied (also for B^{p}). The bracket (17) clearly inherits all the properties of the original Poisson bracket, including the Jacobi identity. Also the degeneracy of entropy is inherited by the constrained Poisson bracket.

To verify that the Lagrange-multiplier construction reproduces the Dirac bracket (12), one should realize that Eqs. (15) and (16) imply the representation

$$\frac{\delta A^{\mathrm{p}}}{\delta x} = (1 - R^{\mathrm{p}} L)\frac{\delta A}{\delta x}. \tag{18}$$

When Eq. (18) and the corresponding representation for B^{p} are inserted into Eq. (17) and the projector property of $R^{\mathrm{p}}L$ is used, we indeed obtain the Dirac bracket (12). The representation (18) still remains to be verified for any observable A^{p} characterized by Eqs. (15) and (16). In geometric terms, Eq. (15) expresses the idea that, on the manifold, the gradient of A can be modified by an arbitrary component normal to the manifold, whereas the component tangential to the manifold remains unchanged. According to Eq. (16), the freedom of choosing the normal component of $\delta A^{\mathrm{p}}/\delta x$ should be used to make the normal component of $L\delta A^{\mathrm{p}}/\delta x$ vanish. This situation is illustrated in Fig. 1. Indeed, Eq. (18) implies

$$\frac{\delta A}{\delta x} - \frac{\delta A^{\mathrm{p}}}{\delta x} = R^{\mathrm{p}} L \frac{\delta A}{\delta x}, \tag{19}$$

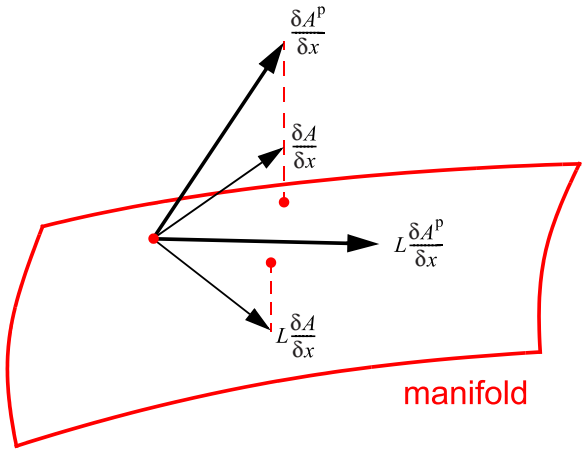

FIG. 1. (Color online) Geometric interpretation of the modification of an observable A into A^{p} such that $L\delta A^{\mathrm{p}}/\delta x$ becomes tangential to the manifold (the small circles indicate points in the manifold, the dashed lines are perpendicular to the manifold).

and hence, in view of the definition (13) of R^{p}, that the difference of the gradients is a linear combination of normal vectors. And in view of the projector property of LR^{p}, the representation (18) moreover implies the condition (16).

B. Irreversible bracket

An irreversible bracket on the submanifold can be constructed by exactly the same ideas employed for the Poisson bracket [19]. Instead of the constrained Poisson bracket (12), we now have

$$[A,B]^{\mathrm{c}} = \frac{\delta A}{\delta x}(M - MR^{\mathrm{d}}M)\frac{\delta B}{\delta x}, \tag{20}$$

where

$$R^{\mathrm{d}}_{jk} = \sum_{\alpha\beta} \frac{\delta\Pi_\alpha}{\delta x_j} J^{\mathrm{d}}_{\alpha\beta} \frac{\delta\Pi_\beta}{\delta x_k}, \tag{21}$$

and $J^{\mathrm{d}}_{\alpha\beta}$ is the inverse of the matrix $[\Pi_\alpha, \Pi_\beta]$. The matrices J^{d} and R^{d} depend on the original irreversible matrix M and on the invariant manifold, but not on the observable A.

For the alternative construction of the constrained irreversible bracket, we start with the modified observables

$$A^{\mathrm{d}}(x) = A(x) + \sum_\alpha \bar\lambda_\alpha^A(x)\Pi_\alpha(x), \tag{22}$$

where the new set of Lagrange multipliers $\bar\lambda_\alpha^A(x)$ must now be chosen such that

$$\frac{\delta\Pi_\alpha}{\delta x} M \frac{\delta A^{\mathrm{d}}}{\delta x} = 0, \tag{23}$$

for all α as an identity on the manifold. In general, the Lagrange multipliers $\bar\lambda_\alpha^A$ are not unique. If suitably modified observables can be constructed, the constrained irreversible bracket is defined by

$$[A,B]^{\mathrm{c}} = [A^{\mathrm{d}}, B^{\mathrm{d}}] = \frac{\delta A^{\mathrm{d}}}{\delta x} M \frac{\delta B^{\mathrm{d}}}{\delta x}, \tag{24}$$

where we have the formal representation

$$\frac{\delta A^{\rm d}}{\delta x} = (1 - R^{\rm d} M)\frac{\delta A}{\delta x}. \tag{25}$$

On the manifold, $[A,B]^{\rm c}$ is independent of the modifications $A^{\rm d}$ and $B^{\rm d}$ of the form (22) as long as the conditions (23) are satisfied (also for $B^{\rm d}$). Moreover, the degeneracy of energy is inherited by the constrained irreversible bracket. In conclusion, the entire GENERIC structure is preserved for the time evolution on the invariant manifold.

C. Alternative procedure

If the number of constraints is small, the linear system associated with the determination of the Lagrange multipliers $\bar{\lambda}^A_\alpha$ from Eq. (23) or the matrix inversion to obtain $J^{\rm d}_{\alpha\beta}$ in Eq. (21) is a small problem. However, when a large fraction of the degrees of freedom is constrained, it may actually be more convenient to focus on the remaining unconstrained degrees of freedom. This can be done in terms of the parametrization $x(y)$ of the invariant manifold. We explain the basic idea in the context of irreversible brackets (the reversible bracket can be discussed in an analogous way).

The geometric content of the construction of constrained brackets is recognized most easily in the Lagrange-multiplier approach. Equations (22) and (23) imply that suitable normal components of $\delta A^{\rm d}/\delta x$ are introduced such that $M\,\delta A^{\rm d}/\delta x$ becomes tangential to the manifold (compare also Fig. 1). By representing $M\,\delta A^{\rm d}/\delta x$ in terms of the tangent vectors $\partial x(y)/\partial y$ and requiring that the tangential components of $\delta A^{\rm d}/\delta x$ coincide with those of $\delta A/\delta x$, we obtain the following alternative procedure. First calculate the matrix

$$K_{\mu\nu} = \sum_{jk} \frac{\partial x_j(y)}{\partial y_\mu} M^{-1}_{jk} \frac{\partial x_k(y)}{\partial y_\nu}, \tag{26}$$

and then find the reduced friction matrix by matrix inversion,

$$\bar{M} = K^{-1}. \tag{27}$$

In practice, instead of calculating the matrix K according to Eq. (26), one can solve the problem

$$M a_\nu = \frac{\partial x(y)}{\partial y_\nu} \tag{28}$$

to obtain a_ν for each tangent vector ν and then evaluate

$$K_{\mu\nu} = \frac{\partial x(y)}{\partial y_\mu} a_\nu. \tag{29}$$

Once the reduced friction matrix $\bar{M}$ has been found, the constrained irreversible bracket is given by

$$[A,B]^{\rm c} = \frac{\delta \bar{A}}{\delta y} \bar{M} \frac{\delta \bar{B}}{\delta y}. \tag{30}$$

The matrix $\bar{M}$ includes the indirect effects from the supplemented normal components of the geometric construction illustrated in Fig. 1. The matrix $\bar{L}$ and the constrained Poisson bracket can be constructed in a fully analogous way.

For a proof of the validity of the alternative procedure, we start from the following representation in terms of tangential vectors,

$$\sum_k M_{jk} \frac{\delta A^{\rm d}}{\delta x_k} = \sum_\nu \frac{\partial x_j(y)}{\partial y_\nu} X^A_\nu. \tag{31}$$

The coefficients X^A_ν can be determined from a set of linear equations after multiplying Eq. (31) by M^{-1},

$$\frac{\delta A^{\rm d}}{\delta x_j} = \sum_{k\nu} M^{-1}_{jk} \frac{\partial x_k(y)}{\partial y_\nu} X^A_\nu, \tag{32}$$

and projecting the result on the tangential vectors $\partial x(y)/\partial y_\mu$,

$$\sum_\nu K_{\mu\nu} X^A_\nu = \sum_j \frac{\delta A^{\rm d}}{\delta x_j} \frac{\partial x_j(y)}{\partial y_\mu} = \frac{\delta \bar{A}}{\delta y_\mu}. \tag{33}$$

For the last step, Eq. (9) has been used, together with the fact that the tangential components of the gradients of A and $A^{\rm d}$ coincide. With the following more explicit version of the representation (32),

$$\frac{\delta A^{\rm d}}{\delta x_j} = \sum_{k\nu\nu'} M^{-1}_{jk} \frac{\partial x_k(y)}{\partial y_\nu} K^{-1}_{\nu\nu'} \frac{\delta \bar{A}}{\delta y_{\nu'}}, \tag{34}$$

the constrained bracket (24) can now be evaluated to obtain Eq. (30).

In our formulation of the alternative procedure, we have used the inverse M^{-1}, although M is degenerate. Equation (28) shows that our procedure requires that the tangent space of the invariant manifold is contained in the image space of M. If that is not the case, $\bar{M}$ should be constructed only on the intersection of the tangent space and the image space of M.

D. Time-evolution equation

The evolution equation resulting from the model reduction implied by an invariant manifold is given by

$$\frac{dx}{dt} = L\frac{\delta E^{\rm p}}{\delta x} + M\frac{\delta S^{\rm d}}{\delta x}, \tag{35}$$

where, for any observable A, both $L\,\delta A^{\rm p}/\delta x$ and $M\,\delta A^{\rm d}/\delta x$ are constructed to be tangential to the manifold. Equation (35) hence describes evolution in the manifold and implies equivalent evolution equations for the intrinsic coordinates y, which inherit the full thermodynamic structure and can be written as

$$\frac{dy}{dt} = \bar{L}\frac{\delta \bar{E}}{\delta y} + \bar{M}\frac{\delta \bar{S}}{\delta y}. \tag{36}$$

Let us look more closely at the irreversible contribution to Eq. (35) (the reversible contribution can be discussed in an analogous way). In general, $\delta S^{\rm d}/\delta x$ is not tangential to the manifold but, by construction, $M\,\delta S^{\rm d}/\delta x$ is. That is, irreversible dynamics along the invariant manifold is not directly generated by the tangential components of $\delta S/\delta x$. However, indirectly it is. Given the tangential components, we have to construct the corresponding normal components to obtain the proper generator $S^{\rm d}$. As the equations for the Lagrange multipliers are linear, we expect the normal components of $\delta S^{\rm d}/\delta x$ to be linear functions of the tangential components, and this is how complicated irreversible behavior can develop in model reduction. Equation (25) nicely shows

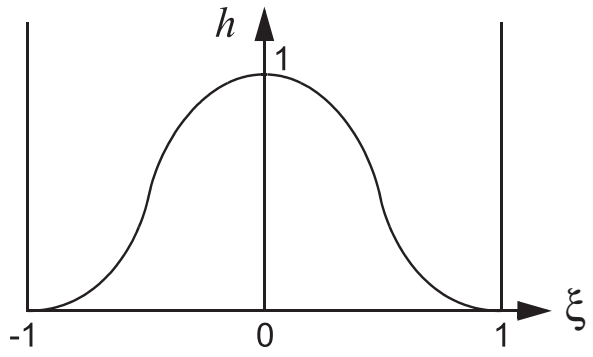

FIG. 2. Normalized double-well potential.

the direct and indirect effects when irreversible dynamics is generated by the tangential components of the entropy gradient. The indirect effect is also included in the reduced friction matrix $\bar{M}$ given by Eq. (27), so that it may develop some nontrivial features.

IV. KRAMERS' ESCAPE PROBLEM

We now illustrate the general thermodynamically consistent model-reduction procedure of the previous section for a simple diffusion problem studied in a classical paper by Kramers [23]. In spite of its simplicity, the problem has some highly relevant features: (i) model reduction leads from linear to nonlinear irreversible thermodynamics, and (ii) the problem can serve as a toy model of chemical reactions, which are of great practical interest.

A. Basic equations and invariant manifold

We study the one-dimensional Fokker-Planck or diffusion equation for a potential barrier separating two minima as shown in Fig. 2. We assume that the potential $h(\xi)$ is a symmetric function with minima at the boundaries $\xi = \pm 1$ and a maximum at $\xi = 0$. For simplicity, we assume $h(\pm 1) = 0$, $h'(\pm 1) = 0$ and $h(0) = 1$. More general functions $h(\xi)$ are discussed in Sec. 3.3 of [24]. The Fokker-Planck equation for the probability density $p = p(\xi,t)$ is given by

$$\frac{\partial p}{\partial t} = D\frac{\partial}{\partial \xi}\left(p\frac{\partial h_\epsilon}{\partial \xi} + \frac{\partial p}{\partial \xi}\right), \tag{37}$$

where D is a constant diffusion coefficient and we have introduced the potential $h_\epsilon = h/\epsilon$ so that we can discuss the limit of a very high potential barrier with activation energy $1/\epsilon$ in the limit $\epsilon \to 0$. Actually, D defines the inverse time scale of our diffusion problem. We further assume impenetrable walls at $\xi = \pm 1$, that is, the probability flux, or the expression in parentheses in Eq. (37), vanishes at the boundaries. The problem of interest is to find the rate at which transitions between the two wells occur for high barriers, which is known as the Kramers escape problem [23].

The equilibrium solution of Eq. (37) is given by

$$p_{\rm eq}(\xi) = \frac{e^{-h_\epsilon(\xi)}}{Z}, \quad Z = \int_{-1}^{1} e^{-h_\epsilon(\xi)}\, d\xi. \tag{38}$$

For the relative deviation from equilibrium, $u = p/p_{\rm eq}$, we obtain the simpler diffusion equation

$$\frac{\partial u}{\partial t} = De^{h_\epsilon}\frac{\partial}{\partial \xi}\left(e^{-h_\epsilon}\frac{\partial u}{\partial \xi}\right). \tag{39}$$

By introducing a rescaled spatial variable $s = s(\xi)$ with

$$\frac{ds}{d\xi} = e^{h_\epsilon}, \quad \frac{d\xi}{ds} = e^{-h_\epsilon}, \tag{40}$$

or

$$s(\xi) = \int_0^\xi e^{h_\epsilon(\xi')}\, d\xi', \tag{41}$$

the diffusion equation (39) for $u = u(s,t)$ becomes even simpler,

$$\frac{\partial u}{\partial t} = De^{2h_\epsilon}\frac{\partial^2 u}{\partial s^2}, \tag{42}$$

with impenetrable walls at the boundaries $s = \pm\hat{s}$ where $\hat{s} = s(1)$. The definition (38) of Z can be rewritten as

$$\int_{-\hat{s}}^{\hat{s}} e^{-2h_\epsilon}\, ds = Z, \tag{43}$$

and the normalization condition for p is turned into the constraint

$$\int_{-\hat{s}}^{\hat{s}} e^{-2h_\epsilon}\, u\, ds = Z. \tag{44}$$

In the limit of small ϵ, $\hat{s}$ is dominated by the behavior of $h_\epsilon(\xi)$ around the maximum. By means of the saddle-point approximation, we find

$$\hat{s} = \frac{1}{2}\int_{-1}^{1} e^{h_\epsilon(\xi)}\, d\xi \approx \sqrt{\frac{\pi\epsilon}{2|h''(0)|}}\, e^{1/\epsilon}. \tag{45}$$

On the other hand, the integral defining Z is dominated by the behavior of $h_\epsilon(\xi)$ near the boundaries and we find

$$Z \approx \sqrt{\frac{2\pi\epsilon}{h''(1)}}. \tag{46}$$

In the same limit, the strongly peaked nature of $\exp\{-2h_\epsilon(s)\}$ implies the following leading-order terms for its integrals,

$$\int_0^{\hat{s}} e^{-2h_\epsilon(s)} f(s)\, ds = \frac{1}{2} f(\hat{s}) Z, \tag{47}$$

and

$$\int_0^{\hat{s}} ds\, e^{-2h_\epsilon(s)} \int_s^{\hat{s}} ds'\, e^{-2h_\epsilon(s')} f(s,s') = \frac{1}{8} f(\hat{s},\hat{s}) Z^2, \tag{48}$$

where f is a sufficiently regular function of one or two arguments. The last two formulas follow from the fact that the symmetric function $\exp\{-2h_\epsilon(s)\}$ with the normalization (43) approximates a δ function.

The diffusion equation in its simplest form (42) shows that the properly normalized affine functions

$$u_y(s) = 1 + ys \tag{49}$$

play a special role as stationary solutions. They correspond to a constant flux through the system and, strictly speaking, are inconsistent with the boundary conditions, except for the

equilibrium distribution with $y = 0$. However, through the potential barrier, that is, away from the boundaries, constant-rate solutions play a key role in Kramers' original solution of the escape problem [23]. In a more rigorous mathematical treatment of the Kramers escape problem [25,26], the functions u_y are equally important as the minimizers in a variational calculation of the integrand of an action, which can alternatively be obtained from the large-deviation principle.

In our approach, the affine functions (49) provide the one-dimensional approximately invariant manifold for a massive model reduction of the diffusion problem. Note that the points x of Sec. III in our example are relative probability densities $u(s)$ and the invariant manifold $x(y)$, which here is one dimensional, is hence given in the form $u_y(s)$. The big problem of finding a suitable invariant manifold is solved by considering the manifold of steady-state solutions. These are the constant-rate solutions that play a key role in Kramers' original work.

B. Diffusion as gradient flow

As a consequence of the absence of a reversible contribution in the diffusion equation (42), the GENERIC framework leads to a formulation as a gradient system. To keep the discussion as simple as possible, we do not include a heat bath which, strictly speaking, would be required to implement the second degeneracy requirement in Eq. (2) expressing energy conservation. The entropy is given by

$$S = -k_{\mathrm{B}} \int_{-1}^{1} p \ln(p/p_{\mathrm{eq}})\, d\xi = -\frac{k_{\mathrm{B}}}{Z} \int_{-\hat{s}}^{\hat{s}} e^{-2h_\epsilon}\, u \ln u\, ds, \tag{50}$$

with the gradient

$$\frac{\delta S}{\delta u} = -\frac{k_{\mathrm{B}}}{Z} e^{-2h_\epsilon} \ln u, \tag{51}$$

where, in view of the normalization constraint (44), the derivative $1 + \ln u$ of $u \ln u$ has been simplified to $\ln u$. With the friction operator

$$M = -\frac{ZD}{k_{\mathrm{B}}} e^{2h_\epsilon} \frac{\partial}{\partial s} u \frac{\partial}{\partial s} e^{2h_\epsilon} \tag{52}$$

we reproduce the diffusion equation (42). In spite of the logarithmic nature of the entropy and the entropy gradient (51), the resulting diffusion equation (42) generated by the entropy gradient is linear in u because the factor u in the friction matrix (52) cancels the factor $1/u$ arising from the derivative of the $\ln u$ with respect to s. More generally, from a thermodynamic perspective, such a fortuitous cancellation is the origin of linearity of all Fokker-Planck equations modeling classical dissipative behavior. It has been pointed out within the GENERIC approach to quantum dissipation that such a cancellation is prevented by operator-ordering problems so that the resulting thermodynamic quantum master equation is intrinsically nonlinear [27–29].

The total entropy production rate (5) is given by

$$\frac{dS}{dt} = \frac{Dk_{\mathrm{B}}}{Z} \int_{-\hat{s}}^{\hat{s}} \frac{1}{u} \left(\frac{\partial u}{\partial s}\right)^2 ds. \tag{53}$$

When evaluated in the manifold (49), the result for the entropy production is

$$\frac{dS}{dt} = \frac{Dk_{\mathrm{B}}}{Z}\, y\, \ln \frac{1 + y\hat{s}}{1 - y\hat{s}} = \frac{Dk_{\mathrm{B}}}{2Z\hat{s}} (u^{\mathrm{R}} - u^{\mathrm{L}})(\ln u^{\mathrm{R}} - \ln u^{\mathrm{L}}), \tag{54}$$

with the left and right boundary values $u^{\mathrm{L}} = u(-\hat{s})$ and $u^{\mathrm{R}} = u(\hat{s})$. The entropy production is always positive (for $u^{\mathrm{R}} \neq u^{\mathrm{L}}$) or zero (for $u^{\mathrm{R}} = u^{\mathrm{L}}$). This is consistent with the more general formula given in Eq. (53), according to which zero entropy production is reached for constant $u(s)$.

For later reference, we evaluate the entropy (50) and its gradient on the manifold of affine functions (49). For small ϵ, the exponential factor in Eq. (50) is very small except in the neighborhood of $\pm\hat{s}$. For any slowly varying function $u(s)$, in particular, for any affine function, the integral in Eq. (50) is hence given by

$$S = -\frac{k_{\mathrm{B}}}{2} (u^{\mathrm{L}} \ln u^{\mathrm{L}} + u^{\mathrm{R}} \ln u^{\mathrm{R}}), \tag{55}$$

where Eq. (47) has been used. Within the manifold given in Eq. (49), we obtain $\bar{S}(y)$ from Eq. (55) and hence the entropy gradient

$$\frac{\partial \bar{S}(y)}{\partial y} = \frac{k_{\mathrm{B}}\hat{s}}{2} (\ln u^{\mathrm{L}} - \ln u^{\mathrm{R}}) = \frac{k_{\mathrm{B}}\hat{s}}{2} \ln \frac{1 - y\hat{s}}{1 + y\hat{s}}. \tag{56}$$

The same result can be obtained from the general chain rule (9) which, for our diffusion problem with a one-dimensional invariant manifold, reads

$$\frac{\partial \bar{A}(y)}{\partial y} = \int_{-\hat{s}}^{\hat{s}} s \frac{\delta A}{\delta u(s)}\, ds. \tag{57}$$

C. Construction of constrained friction matrix

In applying the alternative procedure of Sec. III C to construct the friction matrix resulting from model reduction, we need to consider only a single tangent vector. According to Eq. (28) for the tangent vector $\partial u_y(s)/\partial y = s$ obtained from Eq. (49), we consider the problem

$$\hat{M} a(s) = s, \tag{58}$$

with the normalized diffusion operator

$$\hat{M} = e^{2h_\epsilon} \frac{\partial}{\partial s} u \frac{\partial}{\partial s} e^{2h_\epsilon}. \tag{59}$$

According to Eqs. (27) and (29), the 1×1 friction matrix of the reduced system then is given by

$$\bar{M} = -\frac{ZD}{k_{\mathrm{B}}} \left[\int_{-\hat{s}}^{\hat{s}} s a(s) ds\right]^{-1}. \tag{60}$$

The most general solution of Eq. (58) is given by

$$a(s) = \frac{1}{y} e^{-2h_\epsilon(s)} \left[\ln(1 + ys) \int_c^s s' e^{-2h_\epsilon(s')} ds' - \int_{c'}^s s' \ln(1 + ys') e^{-2h_\epsilon(s')} ds'\right], \tag{61}$$

with the integration constants c and c', as can be verified by applying $\hat{M}$ and assuming u to be of the form (49). We first

choose c' by assuming that, for $y = 0$, the function $a(s)$ should have well-defined symmetry. This assumption requires $c' = 0$, resulting in antisymmetry of $a(s)$. The choice of c' actually has no influence on the friction matrix (60). If we chose also $c = 0$, the formula (47) would imply that $a(s)$ vanishes to leading order. Therefore, the remaining natural choices for c are $\hat{s}$ or $-\hat{s}$, which both lead to the same function $a(s)$. We hence choose

$$c = -\hat{s}, \quad c' = 0, \tag{62}$$

in Eq. (61) to obtain a unique function $a(s)$. Splitting the first integral in Eq. (61) from $c = -\hat{s}$ to s into integrals from $c = -\hat{s}$ to 0 and from 0 to s, the leading-order behavior of the latter integral is canceled by the second integral with $c' = 0$ and we obtain the simple approximate result

$$a(s) = -\frac{Z\hat{s}}{2}\frac{1}{y}\ln(1+ys)\,e^{-2h_\epsilon(s)}, \tag{63}$$

where Eq. (47) has been used. For small ϵ, this function has sharp peaks at $s = \pm\hat{s}$. In the limit $\epsilon \to 0$, we can hence write

$$a(s) = -\frac{Z^2\hat{s}^2}{2}\frac{\delta(s-\hat{s})\ln u^{\mathrm{R}} + \delta(s+\hat{s})\ln u^{\mathrm{L}}}{u^{\mathrm{R}} - u^{\mathrm{L}}}, \tag{64}$$

where we have used the convention that a δ function contributes with full weight if it occurs at the limit of an integration. From Eq. (63) or (64), we obtain

$$\int_{-\hat{s}}^{\hat{s}} sa(s)ds = -\frac{Z^2\hat{s}^3}{2}\frac{\ln u^{\mathrm{R}} - \ln u^{\mathrm{L}}}{u^{\mathrm{R}} - u^{\mathrm{L}}}, \tag{65}$$

and hence from Eq. (60),

$$\bar{M} = \frac{2D}{k_{\mathrm{B}}Z\hat{s}^3}\frac{u^{\mathrm{R}} - u^{\mathrm{L}}}{\ln u^{\mathrm{R}} - \ln u^{\mathrm{L}}}. \tag{66}$$

The equation of motion resulting from the friction matrix (66) and the entropy gradient (56) according to GENERIC (36) is

$$\dot{y} = -\frac{D}{Z\hat{s}^2}(u^{\mathrm{R}} - u^{\mathrm{L}}), \tag{67}$$

or

$$\dot{u}^{\mathrm{R}} = -\dot{u}^{\mathrm{L}} = -\frac{D}{Z\hat{s}}(u^{\mathrm{R}} - u^{\mathrm{L}}). \tag{68}$$

Equation (68) has the structure of a simple example of chemical reaction kinetics. In various thermodynamic approaches to chemical reactions, objects closely related to $\bar{M}$ have been found (see, for example, Eqs. (8) and (9) of Ref. [30], ch. 12 of Ref. [31], Eq. (113) of Ref. [7], Eq. (3.2) of Ref. [32], Sec. 1.8 of Ref. [25], and Eq. (12) of Ref. [33]).

The simplicity of the evolution equation (68) arises because $\bar{M}$ cancels the difference of logarithms resulting from the entropy gradient and replaces it by the difference of the arguments of the logarithms. Such a cancellation mechanism may appear to be unsatisfactory as it removes the effect of the entropy gradient. However, we have constructed $\bar{M}$ by means of a straightforward model reduction procedure. Moreover, the evolution equation (68), together with the expressions (45) and (46) for $\hat{s}$ and Z, coincide with Eqs. (1.4) and (1.5) of Ref. [25].

How does the cancellation mechanism in the friction matrix (66) arise? It can be traced back to the corresponding inverse factor in Eq. (65) and hence to the factor $(1/y)\ln(1+ys)$ in Eq. (63). The latter factor arises from the integration of $1/(1+ys)$ in inverting the operator $\hat{M}$ in Eq. (59) with u of the affine form (49). In other words, the cancellation indeed is a straightforward result of the general reduction procedure for the friction matrix. This factor arises in the construction of the constrained functional derivative of any observable and has nothing to do with the special logarithmic from of the entropy. The cancellation mechanism has *not* been built in artificially to remove the entropy gradient and to obtain the desired evolution equation. Note that the cancellation ultimately arises from the factor u in the diffusion operator (52) or (59). According to the comments after Eq. (52), the fortuitous cancellation leading to linear diffusion equations results from the same factor u in the diffusion operator. In that sense, the cancellation mechanism eliminating logarithms from the master equation (68) is inherited from the mechanism that eliminates logarithms from the diffusion equation (42). As pointed out before, the cancellation mechanism occurring for diffusion equations does not work in quantum dissipation. It has moreover been noticed that a factor of the form $(u^{\mathrm{R}} - u^{\mathrm{L}})/(\ln u^{\mathrm{R}} - \ln u^{\mathrm{L}})$ plays an important role in the discussion of thermodynamic quantum master equations (see Eq. (6) in Ref. [27], Eqs. (16)–(18) in Ref. [28], and Eq. (4.3) in Ref. [34]).

The total entropy production rate (5) calculated from the friction matrix (66) and the entropy gradient (56) coincides with the previous result (54). The model reduction procedure does not change the entropy production rate. This is actually a characteristic hallmark of model reduction, distinguishing it from coarse graining. Whenever degrees of freedom are eliminated by a coarse-graining procedure, additional entropy production arises from the rapid fluctuations associated with the eliminated degrees of freedom (see comments on pp. 210 and 257 of Ref. [8] and the entire conference proceedings volume [35] dedicated to this distinction).

The fact that we reproduce the correct entropy production rate confirms our choice $c = -\hat{s}$ in Eq. (62). For any other choice $-\hat{s} < c < \hat{s}$, the functional form (66) of the friction matrix $\bar{M}$ would remain unchanged, but the friction matrix and hence the entropy production rate would be enhanced by a numerical prefactor which, as discussed in the preceding paragraph, is inappropriate for a model-reduction procedure.

V. SUMMARY

We have adopted the GENERIC framework to define thermodynamically admissible evolution equations and we have associated model reduction with the evolution in an invariant manifold. Given a thermodynamically admissible evolution equation and an invariant manifold, we have then formulated a thermodynamically admissible reduced model. The key idea is to construct the corresponding Poisson and irreversible brackets by constraining the original brackets to the invariant manifold.

By applying the general idea to diffusion in a double-well potential with a high potential barrier, we have found the GENERIC building blocks for the master equation describing the transitions between the potential wells occurring on the time scale given by Kramers' escape rate. Both for the original diffusion equation and for the final master equation,

logarithmic terms resulting from the entropy gradient generating the irreversible dynamics are canceled by the friction matrix, so that the resulting equations are linear. We have found that the cancellation mechanism is actually inherited by the master equation through the model-reduction procedure. Whereas the friction matrix for the diffusion equation is linear, the resulting friction matrix for the master equation is highly nonlinear. The seemingly suspicious form of the nonlinear friction matrix involving a factor $(u^{\mathrm{R}} - u^{\mathrm{L}})/(\ln u^{\mathrm{R}} - \ln u^{\mathrm{L}})$ is the result of the need for components of the entropy gradient perpendicular to the manifold to keep the resulting evolution tangential to the manifold.

VI. CONCLUSIONS AND OUTLOOK

The availability of a general model-reduction procedure that preserves thermodynamic structure opens new possibilities in the field of model reduction for dynamic systems because the resulting equations are then guaranteed to be well behaved. The model-reduction procedure proposed in this paper supplements the efforts to develop a coarse-graining procedure that preserves thermodynamic structure [8,36,37] and leads to thermodynamically guided simulation techniques [38].

Both model reduction and coarse graining deal with the elimination of degrees of freedom to simplify a problem, where these strategies are usually followed by disjoint communities. Model reduction is a solution procedure that does not change the entropy production because, in evolution within an invariant manifold, no relevant information is lost in spite of the elimination of degrees of freedom; coarse graining leads to the emergence of additional entropy production by treating fast degrees of freedom as fluctuations accompanied by dissipation, thus leading to the emergence of irreversibility [35]. The proposed model-reduction procedure guarantees the Jacobi identity for the Poisson bracket. In coarse graining, the preservation of the Jacobi identity is a subtle issue that has been related to the preservation of symmetries (see Sec. 6.1.6 of Ref. [8]). Symmetries can also be used for structure-preserving model reduction (see Sec. 10.5 and ch. 13 of Ref, [21]). As the invariant-manifold method, which we have adopted as a basis for our model-reduction procedure, does not lead to additional entropy production or emerging irreversibility, it has been enhanced by following Ehrenfest's idea of coarse graining in Refs. [39–41] (see also ch. 11 of Ref. [5]). Because this alternative approach to coarse graining is still based on an invariant manifold, the construction of a Poisson bracket automatically satisfying the Jacobi identity can be achieved in the same way as in model reduction. One could thus circumvent the need for cumbersome checks of the Jacobi identity [42] or the use of symbolic mathematical tools [43,44].

A seemingly unnatural mechanism for removing the logarithms resulting from entropy gradients has previously been observed in the context of Boltzmann's kinetic equation [45] and other master equations [46]. For the Boltzmann equation, thermodynamically consistent coarse graining based on a Green-Kubo formula actually suggested a different cancellation mechanism with a nonsymmetric friction matrix [47]. It is hence interesting to realize how an unexpected cancellation can arise from model reduction. A nonsymmetric friction matrix has also been anticipated for two coupled nonlinear chemical reactions [48], based on a study of activated transport processes using mesoscopic nonequilibrium thermodynamics [49]. It would hence be interesting to treat the example of two coupled nonlinear chemical reactions by the model-reduction procedure proposed here.

Further model reduction of Boltzmann's kinetic equation to the level of moments is an important problem in the theory of rarefied gas flows [50,51]. The proposed model-reduction procedure suggests that thermodynamic admissibility can be achieved via corresponding invariant manifolds. For ten moments, the manifold of Gaussian probability densities has been considered in Sec. 7.4.3 of Ref. [8], but our results show that the formula (7.149) of Ref. [8] for the Poisson matrix needs to be corrected in the spirit of the Dirac bracket Eq. (12). For 13 moments, the derivation of an entropy [52–54] has actually been achieved by means of a suitable invariant manifold, so that a corresponding Poisson bracket could be constructed.

The invariant manifold for our example of diffusion in a double-well potential consists of affine functions. By generalizing to piecewise linear functions, spline interpolations, or finite-element representations to define invariant manifolds, one can employ the ideas of the present paper to develop structure-preserving numerical methods for space discretization.

The thermodynamically consistent model-reduction procedure provides an explicit construction of the friction matrix for the reduced model. According to the fluctuation-dissipation rule (see Sec. 1.6 of Ref. [55]), the friction matrix then implies the form of the fluctuations for the reduced model. In view of the geometric nature of the construction of the reduced dynamics in the invariant manifold one could also discuss the resulting fluctuations in the manifold and thus check the validity of the fluctuation-dissipation rule after model reduction.

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