GENERIC framework for the Fokker–Planck equation

Miguel Hoyuelos

Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata, Argentina
Instituto de Investigaciones Físicas de Mar del Plata (Consejo Nacional de Investigaciones Científicas y Técnicas), Funes 3350,
7600 Mar del Plata, Argentina

HIGHLIGHTS

- An extension of the GENERIC formalism to open systems is proposed.
- The approach is limited to bulk interactions (boundary effects are neglected).
- Detailed balance in the stationary state is assumed.
- The stationary solution is included in the set of variables.
- That makes it possible to obtain the GENERIC structure for the Fokker–Planck equation.

ARTICLE INFO

ABSTRACT

The GENERIC theory provides a framework for the description of non-equilibrium phenomena in isolated systems beyond local thermal equilibrium and beyond linear non-equilibrium (i.e., linear relations between thermodynamic forces and currents). The framework is applied to a system described by a Fokker–Planck (FP) equation combined with its reservoir. It is shown that chemical reactions (with stationary solution satisfying detailed balance) can be included in the framework.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The description of an isolated system within the framework of the GENERIC theory [1–3] gives a clear picture of the reversible and irreversible aspects of the dynamics and of the role played by the total energy and entropy (for a comparison with the formalism of rational non-equilibrium thermodynamics, see Ref. [4]). The approach is straightforward when expressions for the energy and entropy as functions (or functionals) of the system variables are known. This is not always the case, specially for the entropy. Nevertheless, the theory can be used to establish the conditions that the entropy should fulfil. The GENERIC theory is focused on isolated systems. Extensions to open or driven systems have been proposed [5–7]. In a related approach, Stokes–Dirac structures are used for a systematic treatment of boundary conditions of open systems [8]. Grmela proposed an extended formulation of the GENERIC theory, that includes open systems, and that addresses the problem of systems that cannot be completely understood in terms of a description that involves only one scale [9]. This multiscale approach aims to systems in which a combination of nano, micro and macro scales are present, a situation not uncommon in nano- and bio-engineering. The formulation is based on the introduction of the abstract geometrical structure inspired in classical equilibrium thermodynamics (contact geometry) that leads to a general mesoscopic non-equilibrium theory [10] (see also Ref. [11]).

In Ref. [7], Öttinger develops an extension to open systems that is based on a distinction between bulk and boundary contributions; the system interacts with the external environment through its boundaries. The approach presented here is

E-mail address: hoyuelos@mdp.edu.ar.

less general, but still relevant. I consider a system in contact with one reservoir. The combination of system and reservoir irreversibly evolves to equilibrium. The entropy of the combination is maximum in equilibrium, but not necessarily so for the system's entropy. The interaction between system and reservoir is present at every point of the system, not only at the boundaries. For simplicity, boundary effects are neglected. This kind of interaction can be described by the Fokker–Planck equation with an external potential (and without boundary effects).

The general time-evolution equation for beyond equilibrium systems, or GENERIC, takes a very compact form:

$$\frac{dX}{dt} = L(X) \cdot \frac{\partial E(X)}{\partial X} + M(X) \cdot \frac{\partial S(X)}{\partial X} \tag{1}$$

where X is a set of variables that describe a closed system, $E(X)$ and $S(X)$ are the total energy and entropy, and $L(X)$ and $M(X)$ are the Poisson and friction matrices that represent the reversible and irreversible contributions generated by $E(X)$ and $S(X)$ respectively. For simplicity, it is assumed that X has no spatial dependence (the notation for a non-homogeneous system is introduced in Section 2). The Poisson matrix $L(X)$ must be antisymmetric and the friction matrix $M(X)$ must be symmetric and positive semidefinite. Furthermore, they should satisfy the degeneracy requirements

$$M(X) \cdot \frac{\partial E(X)}{\partial X} = 0, \tag{2}$$

$$L(X) \cdot \frac{\partial S(X)}{\partial X} = 0. \tag{3}$$

These conditions guarantee energy conservation:

$$\frac{dE}{dt} = \frac{\partial E(X)}{\partial X} \cdot L(X) \cdot \frac{\partial E(X)}{\partial X} + \frac{\partial E(X)}{\partial X} \cdot M(X) \cdot \frac{\partial S(X)}{\partial X} = 0,$$

where the first term vanishes because of the asymmetry of $L(X)$ and the second term because of the first degeneracy condition (2). Entropy increase is also obtained:

$$\frac{dS}{dt} = \frac{\partial S(X)}{\partial X} \cdot L(X) \cdot \frac{\partial E(X)}{\partial X} + \frac{\partial S(X)}{\partial X} \cdot M(X) \cdot \frac{\partial S(X)}{\partial X} \geq 0. \tag{4}$$

The first term is zero due to the condition (3), and the inequality comes from the fact that $M(X)$ is positive semidefinite. A further condition on L is the Jacobi identity (see Ref. [3, p. 14]). In Ref. [1, Sec. III B], a formulation of the Fokker–Planck equation in terms of GENERIC is presented. In the derivation of this formulation, a noise term, that plays the role of an external influence, is included. This term has as a consequence that the degeneracy requirement for matrix L is not generally satisfied. One of the main purposes of the present work is to obtain a GENERIC structure for the Fokker–Planck equation in which the degeneracy requirements are fulfilled through an appropriate choice of the state variables, that include information about the external influence.

The conditions on L and M can be transformed into conditions on the derivatives of the entropy. Here, I illustrate this possibility with a not isolated system of the kind mentioned before. It is necessary to include a reservoir in the description. The combination of system and reservoir is isolated, and $E(X)$ and $S(X)$ represent the energy and entropy of this combination. I use some simplifying assumptions in order to keep the description of the combination system-reservoir as simple as possible.

A drift and diffusion system described by a Fokker–Planck equation is analysed in Section 2. One particularly interesting case is the Kramers equation, with a non-Maxwellian moment distribution, because it goes beyond local thermal equilibrium. I show that the conditions on the friction and Poisson matrices can be used to determine a class of functions to which the entropy should belong.

A general reaction system with detailed balance is analysed in Section 3. The GENERIC structure, given by the friction and Poisson matrices, is obtained. It can be combined with the structure of the Fokker–Planck equation to get the GENERIC structure for reaction–diffusion systems. There are several works dealing with gradient structures or variational formulations of related systems [12–17]. See Ref. [18] for a Wasserstein metric approach to the same problems.

The procedure for obtaining the friction matrix is illustrated in Section 4 with a simple example. The conclusions are presented in Section 5.

2. The Fokker–Planck equation

The Fokker–Planck equation for the density $n \in \mathbb{R}$, in a d dimensional space $\mathbf{x} \in \mathbb{R}^d$, is

$$\frac{\partial n}{\partial t} = -\frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{J} \quad \text{with } \mathbf{J} = \mathbf{A}n - \frac{1}{2}\frac{\partial}{\partial \mathbf{x}} \cdot (Bn), \tag{5}$$

where $\mathbf{J} \in \mathbb{R}^d$ is the particle current, $\mathbf{A} \in \mathbb{R}^d$ is the drift vector and $B \in \mathbb{R}^{d \times d}$ is the (positive semidefinite) diffusion matrix. Both $\mathbf{A}$ and B are, in general, functions of $\mathbf{x}$. The space vector $\mathbf{x}$ may include odd variables under time reversal (like momenta). The units of n are number of particles over volume in space $\mathbf{x}$. Units of $\mathbf{J}$: number of particles per unit time per unit area.

Units of $\mathbf{A}$: distance in space $\mathbf{x}$ over time (it is a velocity for position coordinates, or a force for momenta). Units of B: square of distance over time. (In the notation used, it is assumed that when a vector is applied from the left, with the dot operator, it is transposed.) The system evolves irreversibly to the equilibrium solution n_e. The effect of the reservoir is manifested in, for example, the drift term through the interaction with an external potential. The interaction takes place at every point of the system, not at the boundaries. It is assumed that the system is infinite to avoid boundary effects.

It is convenient to introduce the reversible drift [19,20] defined as $\mathbf{v}(\mathbf{x}) = [\mathbf{A}(\mathbf{x}) - T \cdot \mathbf{A}(T \cdot \mathbf{x})]/2$, where $T \in \mathbb{R}^{d \times d}$ is a diagonal matrix with numbers 1 for even variables and -1 for odd variables under time reversal. Using detailed balance conditions [21, p. 148], it can be shown that

$$\mathbf{v} = \mathbf{A} - \frac{1}{2n_e}\frac{\partial}{\partial \mathbf{x}} \cdot (Bn_e).$$

Then we can separate the current in its reversible and irreversible parts:

$$\mathbf{J} = \underbrace{\mathbf{v}n}_{\text{rev.}} - \underbrace{\frac{n_e}{2}B \cdot \frac{\partial n/n_e}{\partial \mathbf{x}}}_{\text{irrev.}}, \tag{6}$$

where the irreversible part can also be identified by the fact that it should be zero when $n = n_e$. The Kramers equation is an example of Fokker–Planck equation with an equilibrium solution for which the current (and $\mathbf{v}$) is different from zero; see, e.g., Ref. [21, p. 155].

I propose the following set of variables to describe the combination of system and reservoir: $X = (n, \epsilon, n_e) \in \mathbb{R}^3$. The total energy density ϵ is included; it is assumed that it is constant in time (this is not the case for the system energy density, but can be assumed so for the combination system-reservoir). The equilibrium solution n_e is also included; it encodes information about the reservoir and its interaction with the system. Therefore, n is the state variable of the system, and $X = (n, \epsilon, n_e)$ is the set of variables that gives a minimal description of the combination system-reservoir.

The evolution equation is

$$\frac{\partial X}{\partial t} = \begin{pmatrix} -\dfrac{\partial}{\partial \mathbf{x}} \cdot (\mathbf{v}n) + \dfrac{\partial}{\partial \mathbf{x}} \cdot \left(\dfrac{n_e}{2}B \cdot \dfrac{\partial n/n_e}{\partial \mathbf{x}}\right) \\ 0 \\ 0 \end{pmatrix}. \tag{7}$$

Note that the only interesting dynamic behaviour is the one of n, the first component of X. The other (constant) variables are included in order to obtain the GENERIC structure, i.e., the friction and Poisson matrices with their corresponding features. Citing Öttinger in Ref. [3, p. 11]: "A crucial part of GENERIC modelling is the choice of the state variables X or, in other words, the definition of a suitable system to describe certain phenomena of interest". The criteria are to keep the description as simple as possible and not to add new dynamics through the evolution of the – needed – additional variables. Nevertheless, it is not difficult to extend the results to the case in which there is a non-homogeneous total energy current $\mathbf{J}_e$ (with reversible and irreversible parts), so that $\frac{\partial \epsilon}{\partial t} = -\nabla \cdot \mathbf{J}_e$.

A related treatment is found in Ref. [17] for the Vlasov–Fokker–Planck equation for the distribution function of a plasma. The authors of Ref. [17] had to face the same problem: what is the set of variables that satisfy the conditions of GENERIC? The original set of variables are the positions and momenta of the charged particles. In this case they obtained an energy-conserving system adding a new variable that represents the energy of the heat bath. In the present approach I had to include two new variables, ϵ and n_e, but the procedure is simpler since they are not time dependent. On the other hand, here the focus is on a general Fokker–Planck equation.

The entropy density s is a function of n and n_e only; it may be a function also of the internal energy u, but it is assumed that $u = u(n, n_e)$ (this is not the case of the total energy ϵ that may include the effect of an external field).

The total entropy and energy are $S = \int s \, \mathrm{d}^d x \in \mathbb{R}$ and $E = \int \epsilon \, \mathrm{d}^d x \in \mathbb{R}$, and their derivatives are

$$\frac{\delta S}{\delta X} = \begin{pmatrix} \dfrac{\partial s}{\partial n} \\ 0 \\ \dfrac{\partial s}{\partial n_e} \end{pmatrix} \quad \text{and} \quad \frac{\delta E}{\delta X} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}. \tag{8}$$

Since the state vector X is space dependent, we have to rewrite Eq. (1) for this case. The first step is to assume that the system is divided in a large number of small cells. The vector X is expanded to include the values in each cell. Its component i has an additional index that indicate the position of the cell: $X_{i,\,\mathbf{x}}$. Element i, j of matrix L has an additional pair of indices: $L_{i,\,j;\mathbf{x},\,\mathbf{x}'}$; it represents the influence of $\frac{\partial E(X)}{\partial X_{j,\,\mathbf{x}'}}$ over $\frac{\partial X_{i,\,\mathbf{x}}}{\partial t}$. In the continuous limit, the general time-evolution equation takes the form:

$$\frac{\partial X(\mathbf{x})}{\partial t} = L(\mathbf{x}, \mathbf{x}') \bullet \frac{\delta E(X)}{\delta X(\mathbf{x}')} + M(\mathbf{x}, \mathbf{x}') \bullet \frac{\delta S(X)}{\delta X(\mathbf{x}')} \tag{9}$$

where the big dot ● means matrix multiplication and integration in the continuous index $\mathbf{x}'$ (notation used in Ref. [3]), and instead of partial derivatives we have functional derivatives.

The friction matrix $M \in \mathbb{R}^{3\times3}$ and the Poisson matrix $L \in \mathbb{R}^{3\times3}$ are obtained as follows.

2.1. Friction matrix

Using the symmetry property of the friction matrix, it takes the form

$$
M(\mathbf{x}, \mathbf{x}') = \begin{pmatrix} M_{11}(\mathbf{x}, \mathbf{x}') & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{10}
$$

It immediately satisfies the degeneracy condition (2). It should also satisfy

$$
\left. \frac{\partial X}{\partial t} \right|_{\text{irrev}} = M(\mathbf{x}, \mathbf{x}') \bullet \frac{\delta S}{\delta X} = \begin{pmatrix} \frac{\partial}{\partial \mathbf{x}} \cdot \left(\frac{n_e}{2} B \cdot \frac{\partial n/n_e}{\partial \mathbf{x}} \right) \\ 0 \\ 0 \end{pmatrix}, \tag{11}
$$

where $\frac{\delta S}{\delta X}$ is evaluated in $\mathbf{x}'$. The dependence of M on $\mathbf{x}$ and $\mathbf{x}'$ should be interpreted as the generalization of the matrix indices to a continuous space. Then, Eq. (11) means that

$$
\int M_{11}(\mathbf{x}, \mathbf{x}') \left. \frac{\partial s}{\partial n} \right|_{\mathbf{x}'} d^d x' = \frac{\partial}{\partial \mathbf{x}} \cdot \left(\frac{n_e}{2} B \cdot \frac{\partial n/n_e}{\partial \mathbf{x}} \right). \tag{12}
$$

The dimensions of M_{11} are particle density squared over entropy over time (entropy is assumed adimensional taking Boltzmann's constant equal to 1). In order to obtain a more general solution for $M_{11}(\mathbf{x}, \mathbf{x}')$, we rewrite this expression as

$$
\int M_{11}(\mathbf{x}, \mathbf{x}') \left. \frac{\partial s}{\partial n} \right|_{\mathbf{x}'} d^d x' = \frac{\partial}{\partial \mathbf{x}} \cdot \left(\frac{n_e}{2f'} B \cdot \frac{\partial f}{\partial \mathbf{x}} \right), \tag{13}
$$

where f is a function of n/n_e. The solution for $M_{11}(\mathbf{x}, \mathbf{x}')$ is

$$
M_{11}(\mathbf{x}, \mathbf{x}') = \frac{f(\mathbf{x}')}{\left. \frac{\partial s}{\partial n} \right|_{\mathbf{x}'}} \frac{\partial}{\partial \mathbf{x}'} \cdot \left[\frac{n_e(\mathbf{x}')}{2f'(\mathbf{x}')} B(\mathbf{x}') \cdot \frac{\partial \delta(\mathbf{x} - \mathbf{x}')}{\partial \mathbf{x}'} \right], \tag{14}
$$

where $f(\mathbf{x}') = f[n(\mathbf{x}')/n_e(\mathbf{x}')]$ and $\delta(\mathbf{x} - \mathbf{x}')$ is the Dirac delta. It can be shown that (14) is solution by replacing it in (13), integrating twice by parts and neglecting boundary terms.

$M_{11}(\mathbf{x}, \mathbf{x}')$ must be positive semidefinite, i.e., it should be possible to write it as[1]:

$$
M_{11}(\mathbf{x}, \mathbf{x}') = \int d^d x'' \, \mathbf{V}(\mathbf{x}, \mathbf{x}'') \cdot \mathbf{V}(\mathbf{x}', \mathbf{x}''), \tag{15}
$$

where $\mathbf{V}(\mathbf{x}, \mathbf{x}'')$ is a vector of, in principle, arbitrary dimension. To get this form, we rewrite (14) as

$$
M_{11}(\mathbf{x}, \mathbf{x}') = \int d^d x'' \, \delta(\mathbf{x}' - \mathbf{x}'') M_{11}(\mathbf{x}, \mathbf{x}'')
$$
$$
= -\int d^d x'' \frac{\partial}{\partial \mathbf{x}''} \left[\delta(\mathbf{x}' - \mathbf{x}'') \frac{f(\mathbf{x}')}{\left. \frac{\partial s}{\partial n} \right|_{\mathbf{x}'}} \right] \cdot \left[\frac{n_e(\mathbf{x}'')B(\mathbf{x}'')}{2f'(\mathbf{x}'')} \right] \cdot \frac{\partial \delta(\mathbf{x} - \mathbf{x}'')}{\partial \mathbf{x}''}. \tag{16}
$$

The only factor that contains $\mathbf{x}$ is $\frac{\partial \delta(\mathbf{x}-\mathbf{x}'')}{\partial \mathbf{x}''}$, and it should be included in $\mathbf{V}(\mathbf{x}, \mathbf{x}'')$. This means that there should be also a factor $\frac{\partial \delta(\mathbf{x}'-\mathbf{x}'')}{\partial \mathbf{x}''}$ for $\mathbf{V}(\mathbf{x}', \mathbf{x}'')$. Taking

$$
\frac{\partial s}{\partial n} = -f \tag{17}
$$

we obtain the desired form with

$$
\mathbf{V}(\mathbf{x}, \mathbf{x}'') = \sqrt{\frac{n_e(\mathbf{x}'')}{2f'(\mathbf{x}'')}} \, C \cdot \frac{\partial \delta(\mathbf{x} - \mathbf{x}'')}{\partial \mathbf{x}''}, \tag{18}
$$

where I have used the fact that $B = C^T \cdot C$ is positive semidefinite and that f satisfies the condition $f' > 0$.

---

[1] A sufficient condition for a matrix M to be positive semidefinite is that it can be written as $M = C \cdot C^T$. The generalization of this condition to continuous indices is $M(\mathbf{x}, \mathbf{x}') = \int d^d x'' V(\mathbf{x}, \mathbf{x}'') V^T(\mathbf{x}'', \mathbf{x}') = \int d^d x'' V(\mathbf{x}, \mathbf{x}'') V(\mathbf{x}', \mathbf{x}'')$. In (15), V was replaced by vector $\mathbf{V}$ using the fact that the sum of positive semidefinite matrices is also positive semidefinite.

In summary, from the conditions for the friction matrix we obtained that $\frac{\partial s}{\partial n}$ is equal to minus a function of n/n_e with positive derivative. So, the entropy density is

$$s(n, n_e) = -n_e F(n/n_e) + F_e(n_e),\tag{19}$$

where $F' = f$, $F'' > 0$, and F_e is a function of n_e.

Using the maximum condition we have that $\frac{\partial s}{\partial n}\big|_{n=n_e} = -F'(1) = 0$. Let us note that, if the constraint $\int n(\mathbf{x})\, \mathrm{d}^d x = $ const. is considered, an arbitrary constant may be added to F' (see Ref. [3, p. 454]).

2.2. Poisson matrix

For the Poisson matrix, I propose:

$$L(\mathbf{x}, \mathbf{x}') = \begin{pmatrix} 0 & n(\mathbf{x}')\mathbf{v}(\mathbf{x}') \cdot \dfrac{\partial \delta}{\partial \mathbf{x}'} & 0 \\[2mm] -n(\mathbf{x})\mathbf{v}(\mathbf{x}) \cdot \dfrac{\partial \delta}{\partial \mathbf{x}} & 0 & -n_e(\mathbf{x})\mathbf{v}(\mathbf{x}) \cdot \dfrac{\partial \delta}{\partial \mathbf{x}} \\[2mm] 0 & n_e(\mathbf{x}')\mathbf{v}(\mathbf{x}') \cdot \dfrac{\partial \delta}{\partial \mathbf{x}'} & 0 \end{pmatrix}\tag{20}$$

where $\delta = \delta(\mathbf{x} - \mathbf{x}')$. It can be shown that L satisfies Jacobi's identity, a condition that should be fulfilled in the GENERIC structure. It is easy to see that the reversible part of the dynamics is given by

$$\frac{\partial X}{\partial t}\bigg|_{\text{rev.}} = L(\mathbf{x}, \mathbf{x}') \bullet \frac{\delta E}{\delta X} = \begin{pmatrix} -\dfrac{\partial}{\partial \mathbf{x}} \cdot (\mathbf{v}n) \\ 0 \\ 0 \end{pmatrix}.\tag{21}$$

From the degeneracy condition (3) we obtain

$$n\mathbf{v} \cdot \frac{\partial}{\partial \mathbf{x}} \frac{\partial s}{\partial n} + n_e \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{x}} \frac{\partial s}{\partial n_e} = 0.\tag{22}$$

From (19) we have that $\frac{\partial s}{\partial n} = -F'$ and $\frac{\partial s}{\partial n_e} = -F + \frac{n}{n_e}F' + F_e'$, and, replacing in (22), we get $F_e'' = 0$. Then, $F_e(n_e) = c_1 n_e + c_2$; constant c_2 can be ignored (it represents a shift in the origin of the entropy) and the term $c_1 n_e$ can be absorbed into $n_e F$, so that

$$s = -n_e F(n/n_e)\tag{23}$$

with $F'(1) = 0$ and $F''(n/n_e) > 0$. Eq. (23) defines a class of functions for the entropy. The function $s = -n\ln(n/n_e) + n$ is one member of the class.

All members have a similar behaviour close to equilibrium:

$$s \propto -\frac{(n - n_e)^2}{n_e}.\tag{24}$$

In summary, matrices M (10) and L (20) satisfy the required conditions to compose a GENERIC structure for the Fokker–Planck equation.

2.3. Reduction to one space variable

The integration in $\mathbf{x}'$, represented by "$\bullet$" in Eq. (9), can be solved integrating by parts and taking advantage of the Dirac deltas that appear in $L(\mathbf{x}, \mathbf{x}')$ and $M(\mathbf{x}, \mathbf{x}')$. The result is a simplified evolution equation that involves only one space variable:

$$\frac{\partial X(\mathbf{x})}{\partial t} = \bar{L}(\mathbf{x}) \cdot \frac{\delta E(X)}{\delta X(\mathbf{x})} + \bar{M}(\mathbf{x}) \cdot \frac{\delta S(X)}{\delta X(\mathbf{x})}.\tag{25}$$

Matrices $\bar{M}(\mathbf{x})$ and $\bar{L}(\mathbf{x})$ are given by

$$\bar{M}(\mathbf{x}) = \begin{pmatrix} -\dfrac{\partial}{\partial \mathbf{x}} \cdot \dfrac{n_e}{2f'} B \cdot \dfrac{\partial}{\partial \mathbf{x}} & 0 & 0 \\[2mm] 0 & 0 & 0 \\[2mm] 0 & 0 & 0 \end{pmatrix}\tag{26}$$

and

$$
\bar{L}(\mathbf{x}) = \begin{pmatrix} 0 & -\dfrac{\partial}{\partial \mathbf{x}} \cdot n\, \mathbf{v} & 0 \\ -n\, \mathbf{v} \cdot \dfrac{\partial}{\partial \mathbf{x}} & 0 & -n_e\, \mathbf{v} \cdot \dfrac{\partial}{\partial \mathbf{x}} \\ 0 & -\dfrac{\partial}{\partial \mathbf{x}} \cdot n_e\, \mathbf{v} & 0 \end{pmatrix}.
\tag{27}
$$

Let us note that the elements are composed of differential operators that act on all terms to the right of them, and that the antisymmetry of $L(\mathbf{x}, \mathbf{x}')$ is not preserved in $\bar{L}(\mathbf{x})$.

3. Chemical reactions

Let us consider a homogeneous system of m reacting species, with densities $\mathbf{n} = (n_1, \dots, n_m) \in \mathbb{R}^m$. There are r possible reactions, with stoichiometric coefficients $\boldsymbol{\alpha}_j \in \mathbb{R}^m$ ($\boldsymbol{\beta}_j \in \mathbb{R}^m$) for the forward (backward) reaction number j. Using the law of mass action, the reaction rate is

$$
J_j = k_{+j}\mathbf{n}^{\boldsymbol{\alpha}_j} - k_{-j}\mathbf{n}^{\boldsymbol{\beta}_j} \quad \text{for } j = 1, \dots, r
\tag{28}
$$

where $\mathbf{n}^{\boldsymbol{\alpha}_j} = n_1^{\alpha_{1j}} \dots n_m^{\alpha_{mj}}$, and k_{+j} and k_{-j} are the forward and backward reaction constants.

The evolution equation for the densities is

$$
\frac{\partial \mathbf{n}}{\partial t} = \mathbf{R}(\mathbf{n}).
\tag{29}
$$

The reaction term $\mathbf{R} \in \mathbb{R}^m$ is given by

$$
\mathbf{R} = \nu \cdot \mathbf{J}
\tag{30}
$$

where $\mathbf{J} \in \mathbb{R}^r$ is the reaction rate vector, and $\nu \in \mathbb{R}^{m \times r}$ is a matrix of stoichiometric coefficients, with components $\nu_{ij} = \beta_{ij} - \alpha_{ij}$. I assume that, in the stationary state, detailed balance is satisfied, i.e., there is a stationary solution $\mathbf{n}_e = (n_{e1}, \dots, n_{em})$ for which $\mathbf{J}(\mathbf{n}_e) = \mathbf{0}$. Using this condition, we can rewrite the reaction rates as

$$
J_j = c_j \left(\frac{\mathbf{n}^{\boldsymbol{\alpha}_j}}{\mathbf{n}_e^{\boldsymbol{\alpha}_j}} - \frac{\mathbf{n}^{\boldsymbol{\beta}_j}}{\mathbf{n}_e^{\boldsymbol{\beta}_j}} \right),
\tag{31}
$$

with $c_j = k_{+j}\mathbf{n}_e^{\boldsymbol{\alpha}_j} = k_{-j}\mathbf{n}_e^{\boldsymbol{\beta}_j} \geq 0$.

The evolution is irreversible and there are not reversible terms into (29) (if time is inverted none of the terms in the right hand side changes sign). This means that the Poisson matrix L is equal to 0 and only the entropy will be relevant in the dynamics description (see (1)). It is possible to derive the GENERIC structure using the variable $X = \mathbf{n} \in \mathbb{R}^m$. Let us note that this reaction system is closed, and the approach of this section is equivalent to Refs. [15,18]. Nevertheless, for a non-homogeneous system with an external potential and diffusion processes, it is necessary to use $X = (\mathbf{n}, \epsilon, \mathbf{n}_e) \in \mathbb{R}^{2m+1}$ and generalize the results of the previous section to a multicomponent system.

The friction matrix $M \in \mathbb{R}^{m \times m}$ is

$$
M = \frac{\mathbf{R} \otimes \mathbf{R}}{\sigma},
\tag{32}
$$

where $\sigma = \mathbf{R} \cdot \frac{\partial S}{\partial \mathbf{n}}$ and $\mathbf{R} \otimes \mathbf{R}$ is a dyadic tensor with components $[\mathbf{R} \otimes \mathbf{R}]_{ij} = R_i R_j$. We have that

$$
\frac{\partial \mathbf{n}}{\partial t} = M \cdot \frac{\partial S}{\partial \mathbf{n}} = \mathbf{R}.
\tag{33}
$$

It is easy to see that σ is equal to the entropy production rate, $\frac{\partial S}{\partial t}$, and that M satisfies the degeneracy condition (2). Since $\mathbf{R} \otimes \mathbf{R}$ is positive semidefinite,[2] the only condition to have M positive semidefinite is $\sigma \geq 0$.

It is known that

$$
S = \sum_i [n_i - n_i \ln(n_i/n_{ei})]
\tag{34}
$$

satisfies $\sigma \geq 0$ for a reaction system with detailed balance [18] The same form of the entropy for a general reaction described by the law of mass action is used in Ref. [22], where also a more detailed theory that includes microscopic fluctuations is

---

[2] Matrix $\mathbf{R} \otimes \mathbf{R}$ is positive semidefinite since, for any vector $\boldsymbol{\xi}$, we have $\boldsymbol{\xi} \cdot \mathbf{R} \otimes \mathbf{R} \cdot \boldsymbol{\xi} = (\mathbf{R} \cdot \boldsymbol{\xi})^2 \geq 0$.

considered. The condition $\sigma \geq 0$ can be proved as follows:

$$\begin{aligned}
\sigma &= \mathbf{J} \cdot v^T \cdot \frac{\partial S}{\partial \mathbf{n}} \\
&= -\sum_{i,j} c_j \left(\frac{\mathbf{n}^{\alpha_j}}{\mathbf{n}_e^{\alpha_j}} - \frac{\mathbf{n}^{\beta_j}}{\mathbf{n}_e^{\beta_j}} \right) (\beta_{ji} - \alpha_{ji}) \ln \frac{n_i}{n_{ei}} \\
&= \sum_j c_j (a_j - b_j) \ln \frac{a_j}{b_j} \geq 0
\end{aligned} \qquad (35)$$

where $i = 1 \ldots m$, $j = 1 \ldots r$, $a_j = \mathbf{n}^{\alpha_j}/\mathbf{n}_e^{\alpha_j}$ and $b_j = \mathbf{n}^{\beta_j}/\mathbf{n}_e^{\beta_j}$.

4. Example

In this section, the preceding procedure is illustrated with a simple example. Let us consider a system in which there are two types of substances: particles A and molecules A_2, with densities n_1 and n_2 respectively. The following reaction takes place

$$A + A \underset{k_-}{\overset{k_+}{\rightleftharpoons}} A_2 \qquad (36)$$

where k_+ and k_- are the forward and backward reaction constants. The reaction rate is $J = k_+ n_1^2 - k_- n_2$. Particles and molecules diffuse with homogeneous diffusion constants D_1 and D_2 respectively, in a one dimensional space of length L. The limit $L \to \infty$ is considered in order to avoid boundary effects. Since the diffusion coefficients are homogeneous and there are not drift currents, there is no external potential and the system is isolated. The motivation of this example is to show the shape of the friction matrix in the present context in a simple situation.

There are not reversible contributions to the dynamics, i.e., the Poisson matrix is zero and the system can be completely described with a friction matrix. In this case, the system's state is given by $X = (n_1, n_2)$ with the evolution equation

$$\frac{\partial X}{\partial t} = \begin{pmatrix} \frac{\partial n_1}{\partial t} \\ \frac{\partial n_2}{\partial t} \end{pmatrix} = \begin{pmatrix} D_1 \frac{\partial^2 n_1}{\partial x^2} + R_1 \\ D_2 \frac{\partial^2 n_2}{\partial x^2} + R_2 \end{pmatrix}, \qquad (37)$$

where the reaction terms are $\mathbf{R} = (R_1, R_2) = (-2J, J)$.

The aim is to rewrite (37) in terms of the friction matrix M and the entropy $S = \int s \, dx$, with $s = -\sum_{i=1}^2 n_{ei} F(n_i/n_{ei})$ and $F(m) = m \ln m - m$, i.e., to obtain the form of Eq. (1) (with $L = 0$). The equilibrium densities, n_{ei}, are obtained from $J(n_{e1}, n_{e2}) = 0$ and the constraint $n_{1e} + 2n_{2e} = \frac{1}{L} \int dx \, (n_1^0 + 2n_2^0)$, where n_i^0 are the (spatial dependent) initial conditions (there is only one solution with physical meaning, i.e., with $n_{ei} \geq 0$).

It is convenient to separate the friction matrix in its diffusion and reaction parts: $M = M_D + M_R \delta(x - x')$. The diffusion part is diagonal:

$$M_D = \begin{pmatrix} M_{D1} & 0 \\ 0 & M_{D2} \end{pmatrix}. \qquad (38)$$

Using Eqs. (16) and (18), we have $M_{Di} = \int dx'' V_i(x, x'') V_i(x', x'')$, with $V_i(x, x'') = \sqrt{\frac{D_i n_i(x'')}{2}} \frac{\partial \delta(x - x'')}{\partial x''}$. This form explicitly shows that M_D is positive semidefinite. We can also write the equivalent expression

$$M_{Di} = -\frac{D}{2} \frac{\partial}{\partial x'} n \frac{\partial \delta(x - x')}{\partial x'}.$$

The reaction part of the friction matrix is given by (see (32)):

$$M_R = \frac{J^2}{\sigma} \begin{pmatrix} 4 & -2 \\ -2 & 1 \end{pmatrix}, \qquad (39)$$

with $\sigma = (k_+ n_1^2 - k_- n_2) \ln \left(\frac{k_+ n_1^2}{k_- n_2} \right) \geq 0$. Both, M_D and M_R are positive semidefinite, therefore M is also positive semidefinite.

A straightforward calculation shows that

$$\frac{\partial X}{\partial t} = M(x, x') \bullet \begin{pmatrix} \frac{\partial s}{\partial n_1(x')} \\ \frac{\partial s}{\partial n_2(x')} \end{pmatrix}, \qquad (40)$$

is the evolution equation (37), where $\frac{\partial s}{\partial n_i} = -\log(n_i/n_{ei})$. Using Eq. (40), the entropy increase is derived:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \begin{pmatrix} \dfrac{\partial s}{\partial n_1(x)} & \dfrac{\partial s}{\partial n_2(x)} \end{pmatrix} \bullet \begin{pmatrix} \dfrac{\partial n_1(x)}{\partial t} \\ \dfrac{\partial n_2(x)}{\partial t} \end{pmatrix}$$

$$= \begin{pmatrix} \dfrac{\partial s}{\partial n_1(x)} & \dfrac{\partial s}{\partial n_2(x)} \end{pmatrix} \bullet M(x, x') \bullet \begin{pmatrix} \dfrac{\partial s}{\partial n_1(x')} \\ \dfrac{\partial s}{\partial n_2(x')} \end{pmatrix} \geq 0. \tag{41}$$

5. Conclusions

One limitation of the approach is that it applies to a system with bulk interaction, and boundary effects are neglected. Another limitation is the detailed balance assumption for the steady state of reacting dissipative systems. This steady state is identified with equilibrium. In general, reaction–diffusion systems do not satisfy detailed balance — an indication of a non-equilibrium situation. The large variety of behaviours that arise in non-equilibrium phase transitions cannot be treated with the present approach. Nevertheless, it is an extension of the GENERIC structure to a limited but still relevant kind of open systems.

A non-isolated system described by a general Fokker–Planck equation and a reaction system with detailed balance were considered. The results for both cases can be combined for the description of reaction–diffusion systems. Using the conditions on the Poisson and friction matrices, appropriate expressions for the entropy are obtained in each case.

The first difficulty of the examples is that they correspond to non-isolated systems, and the GENERIC equation (in its basic formulation) applies to isolated systems. The approach proposed here is to expand the description to system and reservoir including additional variables.

One of the key ideas is to include the stationary solution into the set of variables, since it encodes information about the influence of the reservoir on the system. This information is relevant as long as the stationary solution is not homogeneous. The inclusion of n_e in the description makes it possible to satisfy the degeneracy condition (22) of the Poisson matrix (21) in the case of the Fokker–Planck equation.

Acknowledgement

References

[1] M. Grmela, H.C. Öttinger, Dynamics and thermodynamics of complex fluids: I. Development of a general formalism, Phys. Rev. E 56 (1997) 6620.
[2] M. Grmela, H.C. Öttinger, Dynamics and thermodynamics of complex fluids: II. Illustrations of a general formalism, Phys. Rev. E 56 (1997) 6633.
[3] H.C. Öttinger, Beyond Equilibrium Thermodynamics, John Wiley & Sons, 2005.
[4] W. Muschik, S. Gümbel, M. Kröger, H.C. Öttinger, A simple example for comparing GENERIC with rational non-equilibrium thermodynamics, Physica A 285 (2000) 448–466.
[5] B.J. Edwards, H.C. Öttinger, R. Jongschaap, On the relationships between thermodynamic formalisms for complex fluids, J. Non-Equilib. Thermodyn. 22 (1997) 356–373.
[6] R. Jongschaap, H.C. Öttinger, The mathematical representation of driven thermodynamic systems, J. Non-Newton. Fluid Mech. 120 (2004) 3–9.
[7] H.C. Öttinger, Nonequilibrium thermodynamics for open systems, Phys. Rev. E 73 (2006) 036126.
[8] A.J. van der Schaft, B.M. Maschke, Hamiltonian formulation of distributed-parameter systems with boundary energy flow, J. Geom. Phys. 42 (2002) 166–194.
[9] M. Grmela, Multiscale equilibrium and nonequilibrium thermodynamics in chemical engineering, in: Advances in Chemical Engineering, vol. 39, Elsevier Academic Press, 2010, p. 75.
[10] M. Grmela, Contact geometry of mesoscopic thermodynamics and dynamics, Entropy 16 (2014) 1652–1686.
[11] M. Grmela, Role of thermodynamics in multiscale physics, Comput. Math. Appl. 65 (2013) 1457–1470.
[12] L. Desvillettes, K. Fellner, Exponential decay toward equilibrium via entropy methods for reaction–diffusion equations, J. Math. Anal. Appl. 319 (2006) 157–176.
[13] M. Liero, A. Mielke, Gradient structures and geodesic convexity for reaction–diffusion systems, Phil. Trans. R. Soc. A 371 (2013) 20120346.
[14] M.A. Peletier, D.R. Michiel Renger, M. Veneroni, Variational formulation of the Fokker–Planck equation with decay: a particle approach, Commun. Contemp. Math. 15 (2013) 1350017.
[15] A. Mielke, Thermomechanical modeling of energy-reaction–diffusion systems, including bulk-interface interactions, Discrete Contin. Dyn. Syst. Ser. S 6 (2013) 479–499.
[16] Shui-Nee Chow, Wen Huang, Yao Li, Haomin Zhou, Fokker–Planck equations for a free energy functional or Markov process on a graph, Arch. Ration. Mech. Anal. 203 (2012) 969–1008.
[17] M.H. Duong, M.A. Peletier, J. Zimmer, GENERIC formalism of a Vlasov–Fokker–Planck equation and connection to large-deviation principles, Nonlinearity 26 (2013) 2951.
[18] A. Mielke, A gradient structure for reaction–diffusion systems and for energy-drift-diffusion systems, Nonlinearity 24 (2011) 1329.

[19] N.G. van Kampen, Derivation of the phenomenological equations from the master equation: I. Even variables only, Physica 23 (1957) 707; Derivation of the phenomenological equations from the master equation: II. Even and odd variables, Physica 23 (1957) 816.
[20] R. Graham, H. Haken, Generalized thermodynamic potential for Markoff systems in detailed balance and far from thermal equilibrium, Z. Phys. 243 (1971) 289–302.
[21] C.W. Gardiner, Handbook of Stochastic Methods, Springer Verlag, Berlin, 1985.
[22] M. Grmela, Fluctuations in extended mass-action-law dynamics, Physica D 241 (2012) 976.