

## 7 Quasi-Chemical Representation

### 7.1 Decomposition of Motions, Non-Uniqueness of Selection of Fast Motions, Self-Adjoint Linearization, Onsager Filter, and Quasi-Chemical Representation

In Chap. 5 we have used the second law of thermodynamics, the existence of the entropy, in order to equip the problem of constructing the slow invariant manifolds with a geometric structure. The requirement of the entropy growth (universally, for all reduced models) restricts significantly the form of the projectors (5.25).

In this chapter we introduce a different but equally important argument – the micro-reversibility ( $T$ -invariance), and its macroscopic consequences, the reciprocity relations. As first discussed by Onsager in 1931 [187], the implication of the micro-reversibility is the self-adjointness of the linear approximation of the system (3.1) in the equilibrium  $x^*$ : for any  $z$  and  $p$ ,

$$\langle (D_x J)_{x^*} z | p \rangle_{x^*} \equiv \langle z | (D_x J)_{x^*} p \rangle_{x^*} . \quad (7.1)$$

The main idea in the present chapter is to use the *reciprocity relations* (7.1) for the fast motions. In order to appreciate this idea, we should mention that the decomposition of motions into fast and slow is not unique. Requirement (7.1) for any equilibrium point of fast motions means a selection (filtration) of the fast motions. We term this the *Onsager filter*. Equilibrium points of fast motions are all the points on manifolds of slow motions. Application of the Onsager filter amounts to a distinguished symmetrization of the linearized vector field  $(D_x J)_x$  in the points  $x$  of the slow manifolds.

To begin with, let us remind the standard way of symmetrization: the linear operator  $A$  is decomposed into the symmetric and the skew-symmetric parts,  $A = \frac{1}{2}(A + A^\dagger) + \frac{1}{2}(A - A^\dagger)$ . Here  $A^\dagger$  is adjoint to  $A$  with respect to a fixed scalar product (entropic scalar product in the present context). However, a replacement of an operator with its symmetric part can lead to catastrophic (from the physical standpoint) consequences such as, for example, loss of stability. In order to construct a sensible Onsager filter, we shall use the *quasi-chemical representation*.

The formalism of the quasi-chemical representation is one of the most developed means of modelling, it makes it possible to “assemble” complex

processes out of elementary processes. There exist various presentations of the quasi-chemical formalism. Our presentation here is a generalization of the approach suggested first by Feinberg [243] (see also [81, 242, 244]).

Symbol  $A_i$  (“quasi-substance”) is put into correspondence to each variable  $x_i$ . The *elementary reaction* is defined according to the *stoichiometric equation*,

$$\sum_i \alpha_i A_i \rightleftharpoons \sum_i \beta_i A_i, \quad (7.2)$$

where  $\alpha_i$  (*the loss stoichiometric coefficients*) and  $\beta_i$  (*the gain stoichiometric coefficients*) are real numbers. Apart from the entropy, one has to specify a monotonic function of one variable,  $\Psi(a)$ ,  $\Psi'(a) > 0$ . In particular, the function  $\Psi(a) = \exp(\lambda a)$ ,  $\lambda = \text{const}$ , is encountered oft in applications.

Given the elementary reaction (7.2), one defines the rates of the direct and of the reverse reactions:

$$\begin{aligned} W^+ &= w^* \Psi \left( \sum_i \alpha_i \mu_i \right), \\ W^- &= w^* \Psi \left( \sum_i \beta_i \mu_i \right), \end{aligned} \quad (7.3)$$

where  $\mu_i = \frac{\partial S}{\partial x_i}$ ,  $x^* = \text{const}$ ,  $x^* > 0$ . The rate of the elementary reaction is then defined as  $W = W^+ - W^-$ .

The equilibrium of the elementary reaction (7.2) is given by the following equation:

$$W^+ = W^-. \quad (7.4)$$

Thanks to the strict monotonicity of the function  $\Psi$ , equilibrium of the elementary reaction is reached when the arguments of the functions coincide in equation (7.3), that is, whenever

$$\sum_i (\beta_i - \alpha_i) \mu_i = 0. \quad (7.5)$$

The vector with the components  $\gamma_i = \beta_i - \alpha_i$  is termed the *stoichiometric vector of the elementary reaction*.

Let  $x^0$  be a point of equilibrium of the reaction (7.2). The linear approximation of the reaction rate has a particularly simple form:

$$W(x^0 + \delta) = -w^* \Psi'(a(x^0)) \langle \gamma | \delta \rangle_{x^0} + o(\delta), \quad (7.6)$$

where  $a(x^0) = \sum_i \alpha_i \mu_i(x^0) = \sum_i \beta_i \mu_i(x^0)$ , and  $\langle | \rangle_{x^0}$  is the entropic scalar product in the equilibrium. In other words,

$$(D_x W)_{x^0} = -w^* \Psi'(a(x^0)) \langle \gamma |. \quad (7.7)$$

Let us write down the kinetic equation for the elementary reaction:

$$\frac{dx}{dt} = \gamma W(x) . \quad (7.8)$$

Linearization of this equation at the equilibrium  $x^0$  has the following form:

$$\frac{d\delta}{dt} = -w^* \Psi'(a(x^0)) \gamma \langle \gamma | \delta \rangle_{x^0} . \quad (7.9)$$

That is, the matrix of the linear approximation has the form,

$$K = -k^* |\gamma\rangle \langle \gamma| , \quad (7.10)$$

where

$$k^* = w^* \Psi'(a(x^0)) > 0 ,$$

while the entropic scalar product is taken at the equilibrium point  $x^0$ .

If there are several elementary reactions, then the stoichiometric vectors  $\gamma^r$  and the reaction rates  $W_r(x)$  are specified for each individual reaction, while the kinetic equation is obtained by summing the right hand sides of equation (7.8) for individual elementary reactions,

$$\frac{dx}{dt} = \sum_r \gamma^r W_r(x) . \quad (7.11)$$

Let us assume that under the reversion of the motions, the direct reaction transforms into the reverse reaction. Thus, the  $T$ -invariance of the equilibrium means that it is reached in the point of the *detailed balance*, where all the elementary reaction equilibrate simultaneously:

$$W_r^+(x^*) = W_r^-(x^*) . \quad (7.12)$$

This assumption is nontrivial if vectors  $\gamma^r$  are linearly dependent (for example, if the number of reactions is greater than the number of species minus the number of conservation laws).

One can call the equations of detailed balance (7.12) the “nonlinear Onsager relations”. These equations give us the restrictions on the reaction rates not only near the equilibrium, in the linear approximation, but also far away from the equilibrium. The representation (7.3) is crucial for this continuation of the usual linear Onsager relations from the neighbourhood of the equilibrium point to the whole phase space. The problem of a rigorous foundation of nonlinear Onsager relations [188, 189] remains open, but a recent attempt made by Berdichevsky [190] seems to be promising.

In the detailed balance case, the linearization of equation (7.11) in the neighborhood of  $x^*$  has the following form ( $x = x^* + \delta$ ):

$$\frac{d\delta}{dt} = - \sum_r k_r^* \gamma^r \langle \gamma^r | \delta \rangle_{x^*} , \quad (7.13)$$

where

$$k_r^* = w_r^* \Psi'_r(a_r^*) > 0 ,$$

$$a_r^* = \sum_i \alpha_i^r \mu_i(x^*) = \sum_i \beta_i^r \mu_i(x^*) .$$

The following matrix of the linear approximation is obviously self-adjoint and stable:

$$K = - \sum_r k_r^* |\gamma^r\rangle \langle \gamma^r| . \quad (7.14)$$

Note that matrix  $K$  is the sum of matrices of rank one.

Let us now extract the self-adjoint part of the form (7.14) in the *arbitrary* point  $x$ . Linearizing the reaction rate about  $x$ , we obtain:

$$W(x + \delta) = w^* (\Psi'(a(x)) \langle \alpha | \delta \rangle_x - \Psi'(b(x)) \langle \beta | \delta \rangle_x) + o(\delta) , \quad (7.15)$$

where

$$a(x) = \sum_i \alpha_i \mu_i(x) ,$$

$$b(x) = \sum_i \beta_i \mu_i(x) .$$

Let us introduce notation,

$$k^{\text{SYM}}(x) = \frac{1}{2} w^* (\Psi'(a(x)) + \Psi'(b(x))) > 0 ,$$

$$k^{\text{A}}(x) = \frac{1}{2} w^* (\Psi'(a(x)) - \Psi'(b(x))) .$$

In terms of this notation, equation (7.15) may be rewritten,

$$W(x + \delta) = -k^{\text{SYM}}(x) \langle \gamma | \delta \rangle_x + k^{\text{A}}(x) \langle \alpha + \beta | \delta \rangle_x + o(\delta) . \quad (7.16)$$

The second term vanishes in the equilibrium ( $k^{\text{A}}(x^*) = 0$ , due to the detailed balance).

The *symmetric linearization* (Onsager filter) amounts to keeping only the first term in the linearized vector field (7.16) when studying the fast motion towards the (approximate) slow manifolds, instead of the full expression (7.15). Matrix  $K(x)$  of the linear approximation becomes then similar to (7.14):

$$K(x) = - \sum_r k_r^{\text{SYM}}(x) |\gamma^r\rangle \langle \gamma^r| , \quad (7.17)$$

where

$$k_r^{\text{SYM}}(x) = \frac{1}{2} w_r^* (\Psi'_r(a(x)) + \Psi'_r(b(x))) > 0 ,$$

$$a_r(x) = \sum_i \alpha_i^r \mu_i(x) ,$$

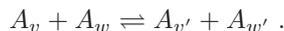
$$b_r(x) = \sum_i \beta_i^r \mu_i(x) ,$$

while the entropic scalar product  $\langle | \rangle_x$  is taken at the point  $x$ . For each label of the elementary reaction  $r$ , the function  $k_r^{\text{SYM}}(x)$  is positive. Thus, the stability of the symmetric matrix (7.17) is elicited.

Symmetric linearization (7.17) is distinguished also by the fact that it preserves the rank of the elementary processes contributing to the complex mechanism. Same as in the equilibrium case, the matrix  $K(x)$  is the sum of rank one operators corresponding to each individual process. This is not so for the standard symmetrization.

Using the symmetric operator (7.17) in the above Newton method with incomplete linearization can be considered as a version of a heuristic strategy of “we act in such a way as if the manifolds  $F(W)$  were already slow invariant manifolds”. If this were the case, then, in particular, the fast motions towards the were described by the self-adjoint linear approximation.

We have described the quasi-chemical formalism for finite-dimensional systems. Infinite-dimensional generalizations are almost straightforward in many important cases, and are achieved by a mere replacement of summation by integration. The best known example is the Boltzmann collision integral: each velocity  $v$  corresponds to a quasi-substance  $A_v$ , and a collision is described by a stoichiometric equation:



In the Example to this chapter we consider the Boltzmann collision integral from this standpoint in a more detail.

## 7.2 Example: Quasi-Chemical Representation and Self-Adjoint Linearization of the Boltzmann Collision Operator

A decomposition of motions near a thermodynamically nonequilibrium states results in a linear relaxation towards this state. In this Example, the linear operator of this relaxation is explicitly constructed in the case of the Boltzmann equation.

Let us remind that the entropy-related specification of the equilibrium state is due to the two points of view. From the first, thermodynamic viewpoint, equilibrium is a state in which the entropy is maximal. From the second, kinetic viewpoint, a quadratic form of the entropy increases in a course of linear regression towards this state. If the underlying microscopic dynamics is time-reversible, the kinetic viewpoint is realized due to the well-known symmetry properties of the linearized kinetic operator.

In a majority of near-equilibrium studies, a principle of a decomposition of motions into fast and slow occupies a distinct place. In some special cases, decomposition of motions is taken into account explicitly, by introducing a small parameter into dynamic equations. More frequently, however, it comes

into play implicitly, for example, through an assumption of a fast decay of memory in the projection operator formalism [194]. Even in presence of long-living dynamic effects (mode coupling), an assumption about decomposition of motions is required as a final instance to obtain a closed set of equations for slow variables.

However, for closed systems, there remains a question: whether and to what extent the two aforementioned entropy-related points of view are applicable to non-equilibrium states? Further, if an answer is affirmative, then how to make explicitly the corresponding specification?

This Example is aimed at answering the questions just mentioned, and it is a straightforward continuation of results [11, 14]. Namely, in [11, 14], it was demonstrated that the principle of motions decomposition alone constitutes a necessary and sufficient condition for the thermodynamic specification of a non-equilibrium state. However, in a general situation, one deals with states  $f$  other than  $f_0$ . A question is, whether these two ideas can be applied to  $f \neq f_0$  (at least approximately), and if so, then how to make the presentation explicit.

The positive answer to this question was partially given in the framework of the method of invariant manifolds [9, 11, 14]. Objects studied in [9, 11, 14] were manifolds in the space of distribution functions, and the goal was to construct iteratively a manifold that is tangent in all its points to a vector field of a dissipative system (an invariant manifold), beginning with some initial manifold with no such property. It was natural to employ methods of KAM-theory (Newton-type linear iterations to improve the initial manifold). However, additional idea of the decomposition of motions into fast and slow near the manifold was required to adapt KAM-theory to dissipative systems. The geometrical formulation of this idea [9, 11, 14] results in a definition of a plane of fast motion,  $\Gamma_f$ , associated with the state  $f$ , and orthogonal to the gradient of the entropy in  $f$ . The physical interpretation of  $\Gamma_f$  is that contains all those states from a neighborhood of  $f$ , which come into  $f$  in the course of fast relaxation (as if  $f$  were the final state of fast processes occurring in its neighborhood). Usually,  $\Gamma_f$  contains more states than can come into  $f$  in a fast relaxation because of the conservation of certain macroscopic quantities (e.g. density, momentum, and energy, as well as, possibly, higher moments of  $f$  which practically do not vary during the fast processes). The redundant states are eliminated by imposing additional restrictions which cut out “thinner” linear manifolds, planes of fast motions  $P_f$ , inside  $\Gamma_f$ . Extremal property of  $f$  on  $\Gamma_f$  is preserved also on  $P_f$  (cf. [9, 11, 14]).

Thus, the decomposition of motions near a manifold results in the thermodynamical viewpoint: the states  $f$  on the manifold are described as the unique points of the entropy maximum of corresponding planes of fast motions  $\Gamma_f$ . This formulation defines a slow dynamics on the manifolds in agreement with the  $H$ -theorem for the Boltzmann equation, or with its analogs for other systems (see [9, 11, 14] for details). As it was demonstrated in [9, 11, 14], the

decomposition of motions in a neighborhood of  $f$  is a criterion (a necessary and sufficient condition) of the existence of the thermodynamic description of  $f$ .

The Newton iteration improves the states of a non-invariant manifold ( $f + \delta f$ ), while  $\delta f$  is thought on  $\Gamma_f$ . Equation for  $\delta f$  involves a linearization of the collision integral in the state  $f$ . Here, if  $f \neq f_0$ , where  $f_0$  is the local equilibrium, we face a problem of how to perform the linearization of the collision integral in concordance with the  $H$ -theorem (corrections to the manifold of local equilibrium states were studied in detail in [11]).

Here we show that the aforementioned assumption about the decomposition of motions results in the kinetic description of states on manifolds of slow motions, and that Onsager's principle can be applied in a natural way to linearize the Boltzmann collision integral.

As it follows from the definition to definition of  $\Gamma_f$ , the state  $f$  is the unique point of minimum of the  $H$ -function on  $\Gamma_f$ . In the first non-vanishing approximation, we have the following expression for the  $H$ -function in the states on  $\Gamma_f$ :

$$H(f + \delta f) \approx H(f) + \frac{1}{2} \langle \delta f | \delta f \rangle_f$$

Here  $\langle \cdot | \cdot \rangle_f$  denotes the scalar product generated by the second derivative of  $H$  in the state  $f$ :  $\langle g_1 | g_2 \rangle_f = \int f^{-1} g_1 g_2 d\mathbf{v}$ .

Decomposition of motions means that the quadratic form  $\langle \delta f | \delta f \rangle_f$  decays monotonically in the course of the linear relaxation towards the state  $f$ . It is natural, therefore, to impose the requirement that this linear relaxation should obey Onsager's principle. Namely, the corresponding linear operator should be symmetric (formally self-adjoint) and non-positively definite with respect to the scalar product  $\langle \cdot | \cdot \rangle_f$ , and furthermore, the kernel of this operator should consist of linear combinations of conserved quantities ( $1$ ,  $\mathbf{v}$ , and  $v^2$ ). In other words, the decomposition of motions should portray the pattern of the linear relaxation in the vicinity of  $f$  similar to that in a small neighborhood of  $f_0$ . Following this idea, we shall now decompose the linearized collision integral  $L_f$  in two parts:  $L_f^{\text{SYM}}$  (satisfying Onsager's principle), and  $L_f^{\text{A}}$  (the non-thermodynamic part).

In the state  $f$ , each direct encounter,  $(\mathbf{v}, \mathbf{v}_1) \rightarrow (\mathbf{v}', \mathbf{v}'_1)$ , together with the reverse encounter,  $(\mathbf{v}', \mathbf{v}'_1) \rightarrow (\mathbf{v}, \mathbf{v}_1)$ , contribute a rate,  $G^+(f) - L^-(f)$  ("gain-loss"), to the collision integral, where (see Chap. 2):

$$W(f) = W(\mathbf{v}', \mathbf{v}'_1; \mathbf{v}, \mathbf{v}_1) \exp \{ D_f H|_{f=f(\mathbf{v})} + D_f H|_{f=f(\mathbf{v}_1)} \};$$

$$W'(f) = W(\mathbf{v}', \mathbf{v}'_1; \mathbf{v}, \mathbf{v}_1) \exp \{ D_f H|_{f=f(\mathbf{v}')} + D_f H|_{f=f(\mathbf{v}'_1)} \};$$

A deviation  $\delta f$  from the state  $f$  will change the rates of both the direct and the reverse processes. Resulting deviations of the rates are:

$$\delta W = W(f) \{ D_f^2 H|_{f=f(\mathbf{v})} \cdot \delta f(\mathbf{v}) + D_f^2 H|_{f=f(\mathbf{v}_1)} \cdot \delta f(\mathbf{v}_1) \};$$

$$\delta W' = W'(f) \{ D_f^2 H|_{f=f(\mathbf{v}')} \cdot \delta f(\mathbf{v}') + D_f^2 H|_{f=f(\mathbf{v}'_1)} \cdot \delta f(\mathbf{v}'_1) \};$$

Symmetrization with respect to the direct and the reverse encounters will give a term proportional to a balanced rate,  $W^{\text{SYM}}(f) = \frac{1}{2}(W(f) + W'(f))$ , in both of the expressions  $\delta W$  and  $\delta W'$ . Thus, we come to the decomposition of the linearized collision integral,  $L_f = L_f^{\text{SYM}} + L_f^{\text{A}}$ , where

$$L_f^{\text{SYM}} \delta f = \int w \frac{f' f'_1 + f f_1}{2} \left\{ \frac{\delta f'}{f'} + \frac{\delta f'_1}{f'_1} - \frac{\delta f_1}{f_1} - \frac{\delta f}{f} \right\} d\mathbf{v}'_1 d\mathbf{v}' d\mathbf{v}_1; \quad (7.18)$$

$$L_f^{\text{A}} \delta f = \int w \frac{f' f'_1 - f f_1}{2} \left\{ \frac{\delta f'}{f'} + \frac{\delta f'_1}{f'_1} + \frac{\delta f_1}{f_1} + \frac{\delta f}{f} \right\} d\mathbf{v}'_1 d\mathbf{v}' d\mathbf{v}_1; \quad (7.19)$$

$f = f(\mathbf{v})$ ,  $f_1 = f(\mathbf{v}_1)$ ,  $f' = f(\mathbf{v}')$ ,  $f'_1 = f(\mathbf{v}'_1)$ ,  $\delta f = \delta f(\mathbf{v})$ ,  $\delta f_1 = \delta f(\mathbf{v}_1)$ ,  $\delta f' = \delta f(\mathbf{v}')$ ,  $\delta f'_1 = \delta f(\mathbf{v}'_1)$ .

Operator  $L_f^{\text{SYM}}$  (7.18) satisfies all the aforementioned requirements pertinent to Onsager's principle, namely:

- (i)  $\langle g_1 | L_f^{\text{SYM}} | g_2 \rangle_f = \langle g_2 | L_f^{\text{SYM}} | g_1 \rangle_f$  (symmetry);
- (ii)  $\langle g | L_f^{\text{SYM}} | g \rangle_f \leq 0$  (local entropy production inequality);
- (iii)  $f, \mathbf{v}f, v^2 f \in \ker L_f^{\text{SYM}}$  (conservation laws).

For an unspecified  $f$ , the non-thermodynamic operator  $L_f^{\text{A}}$  (7.19) has none of these properties. If  $f = f_0$ , then the part (7.19) vanishes, while operator  $L_{f_0}^{\text{SYM}}$  becomes the usual linearized collision integral due to the balance  $W(f_0) = W'(f_0)$ .

The non-negative definite form  $\langle \delta f | \delta f \rangle_f$  decays monotonically due to the equation of linear relaxation,  $\partial_t \delta f = L_f^{\text{SYM}} \delta f$ , and the unique point of minimum,  $\delta f = 0$ , of  $\langle \delta f | \delta f \rangle_f$  corresponds to the equilibrium point of the vector field  $L_f^{\text{SYM}} \delta f$ .

Operator  $L_f^{\text{SYM}}$  describes the state  $f$  as the equilibrium state of the linear relaxation. Note that the method of extracting the symmetric part (7.18) is strongly based on the representation of the direct and the reverse processes, and it is not a simple procedure like, e.g.,  $\frac{1}{2}(L_f + L_f^\dagger)$ . The latter expression cannot be used as a basis for Onsager's principle since it would violate conditions (ii) and (iii).

Thus, if motions do decompose into a fast motion towards the manifold and a slow motion along the manifold, then states on this manifold can be described from both the thermodynamic and the kinetic points of view. Our consideration results in the explicit construction of the operator  $L_f^{\text{SYM}}$  (7.18) responsible for the fast relaxation towards the state  $f$ . It can be used, in particular, for obtaining corrections to such approximations as the Grad moment approximations and the Tamm–Mott–Smith approximation, in the framework of the method of invariant manifold [9, 14, 21]. The non-thermodynamic part (7.19) is always present in  $L_f$ , when  $f \neq f_0$ , but if trajectories of an equation  $\partial_t \delta f = L_f \delta f$  are close to the trajectories of the equation  $\partial_t \delta f = L_f^{\text{SYM}} \delta f$ ,

then  $L_f^{\text{SYM}}$  is a good approximation to  $L_f$ . Statements about closeness of trajectories depend on specific features of  $f$ , and typically they can be claimed when a small parameter is present. On the other hand, the explicit thermodynamic and kinetic presentation of states on a manifold of slow motions (the extraction of  $L_f^{\text{SYM}}$  as above and construction of planes  $\Gamma_f$  [9, 11, 14]) is based just on the assumption about the decomposition of motions, and can be used avoiding a consideration of a small parameter.

