

Thermodynamic field theory: Chemical examples^(*)

PH. PEETERS⁽¹⁾ and G. SONNINO⁽²⁾

⁽¹⁾ *Belgian Institute for Space Aeronomy - 3 Av. Circulaire, B-1180 Brussels, Belgium*

⁽²⁾ *European Commission, Research Directorate - 8 Square de Meeûs*

B-1049, Brussels, Belgium

Instituts Internationaux de Physique et de Chimie Fondé par E. SOLVAY ASBL

50 Av. F.D. Roosevelt, B-1050, Brussels, Belgium

(ricevuto il 5 Giugno 2000)

Summary. — The thermodynamic field theory, exposed in this issue, allows to describe thermodynamic systems, even when evolving far away from equilibrium. More particularly it is shown that far from equilibrium the tensor which relates forces with flows will display a skew-symmetric part. In this work we describe a simple chemical model characterised by the existence of a limit cycle (chemical oscillations). This model allows to compute the generalized flows taking into account Onsager's theory and by making an appropriate choice of fluxes and forces which leaves invariant the expression of the entropy production. We show that the numerical results are in agreement with the theoretical predictions.

PACS 11.10.Kk – Field theories in dimensions other than four.

PACS 05.70.Ln – Nonequilibrium and irreversible thermodynamics.

PACS 01.30.Cc – Conference proceedings.

1. – Introduction

An introductory work on thermodynamic field theory has been published in the present issue [1]. The aim of the work was to evaluate the relation between the generalised thermodynamic forces and their conjugated flows. When the system is below the first instability, it can be shown that the evolution of the thermodynamic system is well described in the space of Riemannian geometry. Beyond the first instability, the property of stationary length cannot be applied since no length is defined in the thermodynamic space. To ensure the validity of the *Universal Criterion of Evolution* which, as known, remains valid even when the system is far from equilibrium, we introduced a thermodynamic space with symmetric connection: the Weyl space.

(*) Paper presented at the III ICRA Network Workshop and VI Italo-Korean Meeting on Electrodynamics and Magnetohydrodynamics around Black Holes, Rome-Pescara, July 12-24, 1999.

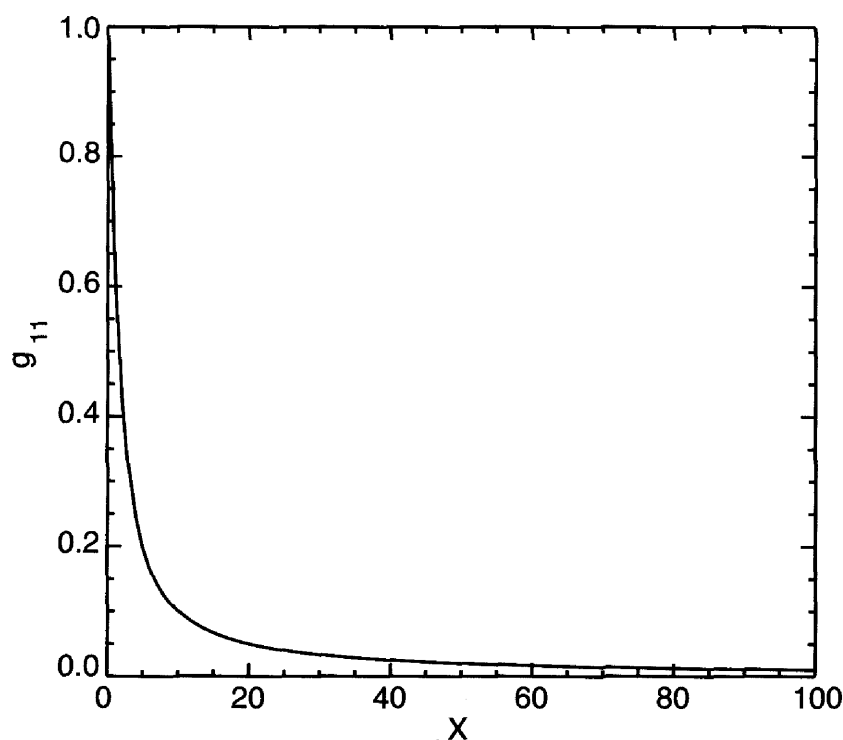


Fig. 1. - Projection of the solution of eq. (1) on the plane $\hat{X}^1 = 0$. This curve coincides with the expression found by De Donder.

As example of application, we treated the *Unimolecular Triangular Reaction* problem. In the limit of weak-field approximation, the field equations read

$$(1) \quad [(h_{\mu\nu})^{\rho}]_{;\rho} = 0.$$

The approximated solution of eq. (1) is

$$(2) \quad \begin{aligned} h_{\mu\nu} &\simeq \hat{L}_{\mu\nu} \frac{1 - e^{-(\Gamma_3 \hat{X}^2 + \hat{X}^1)}}{\Gamma_3 \hat{X}^2 + \hat{X}^1} - L_{\mu\nu}, & \text{if } \frac{\hat{X}^2}{\sqrt{\Gamma^{22}}} < \frac{\hat{X}^1}{\sqrt{\Gamma^{11}}}, \\ h_{\mu\nu} &\simeq \hat{L}_{\mu\nu} \frac{1 - e^{-(\Gamma_1 \hat{X}^1 + \hat{X}^2)}}{\Gamma_1 \hat{X}^1 + \hat{X}^2} - L_{\mu\nu}, & \text{if } \frac{\hat{X}^2}{\sqrt{\Gamma^{22}}} > \frac{\hat{X}^1}{\sqrt{\Gamma^{11}}}, \end{aligned}$$

where $\hat{L}_{\mu\nu}$ is a matrix which, at equilibrium, reduces to the matrix $L_{\mu\nu}$, built up by Onsager's coefficients [1] and $\hat{X}^\mu = X^\mu/R$ (X^μ denote the thermodynamic forces and " R " the *universal constant of gases*). The projection of the solution (2) on the plane $X^1 = 0$, coincides with the expression found by de Donder (see also fig. 1)

$$(3) \quad w_i = \omega_i \left[1 - \exp[-\hat{X}^i] \right] = \omega_i \left[1 - \exp \left[-\frac{A_i}{RT} \right] \right].$$

In this paper, we will analyse in great detail a more complex chemical system near the first instability (chemical oscillations): the Field-Körös-Noyes model. We will show that the numerical solution of the model is in agreement with theoretical predictions.

2. – The Field-Körös-Noyes model

The Field-Körös-Noyes model (FKN) is interesting under various standpoints. First for our purpose the selected model must remain simple and tractable yet still exhibit at least three independent variables. Secondly it must be “interesting” in the framework of the field description of thermodynamic, *i.e.* it must be able to display singular behavior.

In the early and mid 20th century, several experimental works have described chemical systems which, under some carefully chosen conditions, were able to exhibit a periodic behavior in the sense that some chemical concentrations oscillate in time. Most notably, the works of Bray (1928), Belusov (1951-1959) and Zhabotinsky [2] are remarkable in this regard. Using a simple trimolecular model, the so-called *Brusselator*, Prigogine and Lefever [3] show how this kind of behavior is compatible with the thermodynamic far from equilibrium. Later, Field, Körös and Noyes proposed one simplified model of the Belusov and Zhabotinsky reaction whose dynamic is described by three variables.

Without going into the details of the chemical reaction involved, let us just summarize the 5 steps of the model:

(4)	Step		Reaction rate
	$A + Y \rightleftharpoons X + P$		$\omega_1 = k_1 AY - kXP$
	$A + Y \rightleftharpoons 2X + 2Z$		$\omega_2 = k_2 AX - kX^2 Z^2$
	$X + Y \rightleftharpoons 2P$		$\omega_3 = k_3 XY - kP^2$
	$2X \rightleftharpoons A + P$		$\omega_4 = k_4 X^2 - kAP$
	$B + Z \rightleftharpoons \frac{f}{2}Y$		$\omega_5 = k_5 BZ - kY^{f/2}$

To avoid divergence of affinities of the single chemical steps, we have to take into consideration also the reverse steps. Each of them is characterized by the same arbitrary kinetic constant k . Also, for the sake of simplicity, we chose f to be equal to 2. It should also be noted that one of the reverse steps involves a quadrimolecular reaction which is highly unlikely (its probability of occurrence is almost negligible). Additional details and references about this particular reaction can be found in ref. [4].

The thermodynamic equilibrium is defined by the following conditions:

$$(5) \quad k = \frac{k_1 k_4}{k_3},$$

$$(6) \quad P^{7/2} = K_1^2 K_2 K_4^{3/2} K_5^2 B^2,$$

$$(7) \quad X_{eq}^2 = \frac{kAP}{k_4},$$

$$(8) \quad Y_{eq} = k \sqrt{\frac{APk}{k_4}} \frac{P}{k_1 A},$$

$$(9) \quad Z_{eq} = \frac{k^2 P}{k_1 k_5 B} \sqrt{\frac{Pk}{Ak_4}},$$

where the uppercase kinetic constant K_i is simply the reduced constant k_i/k .

For carefully chosen values of the parameters away from equilibrium, this model exhibits an oscillatory behavior. We illustrate this in fig. 2 where the reversible model is

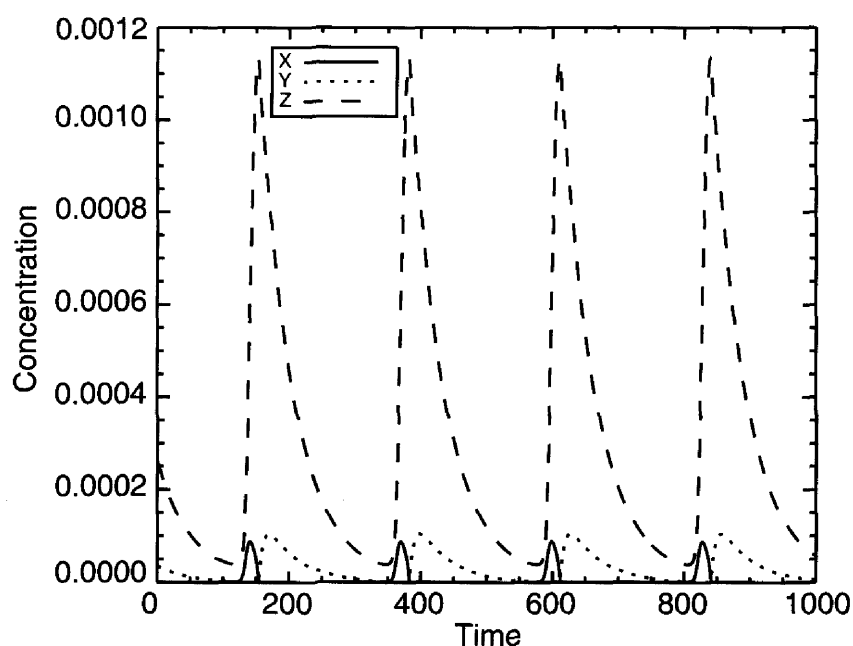


Fig. 2. – Oscillatory behavior of the reversible FKN model (eq. (4)). The concentration of X , Y and Z are shown for the value of parameters given in the text.

numerically integrated using the values of parameters $A = 0.06$, $B = 0.02$, $k_1 = 1.28$, $k_2 = 8$, $k_3 = 8 \times 10^5$, $k_4 = 2 \times 10^3$, $k_5 = 1$, $P = 10^{-3}$ and $k = 0.0032$.

3. – The metric tensor

In this chemical problem, we do not have to solve the field equation for the metric $g_{\mu\nu}$. Equilibrium thermodynamic imposes some conditions to the metric. We know that the metric must reduce to Onsager's tensor at equilibrium. The first step is to correctly define the forces and fluxes. They must be linearly independent. The forces are a suitable linear combination of the chemical affinity while the fluxes will be derived from the corresponding linear combination of reaction rate or velocity.

Following Haase [5], the affinities of the reactions can be expressed in term of the linearly independent generalized forces F_r as

$$(10) \quad A_l = \sum_{r=1}^R b_{rl} F_r,$$

where R is the number of independent forces and l runs from 1 to L , the number of elementary steps. The tensor character of the different quantities will be introduced below. The fluxes (velocity) must then be expressed as

$$(11) \quad v_r = \sum_{l=1}^L b_{rl} \omega_l.$$

The linearly independent velocities are those corresponding to the three independent chemical species X , Y and Z . We finally find that

$$(12) \quad v_1 = \omega_1 + \omega_2 - \omega_3 - 2\omega_4,$$

$$(13) \quad v_2 = -\omega_1 - \omega_3 + \omega_5 ,$$

$$(14) \quad v_3 = 2\omega_2 - \omega_5$$

and, then

$$(15) \quad F^1 = -\frac{1}{2} \frac{A_4}{RT} ,$$

$$(16) \quad F^2 = -\frac{1}{2} \frac{A_4}{RT} - \frac{A_1}{RT} ,$$

$$(17) \quad F^3 = \frac{1}{2} \frac{A_2}{RT} + \frac{1}{4} \frac{A_4}{RT}$$

and the affinity of each step is defined as (see, *e.g.*, [6])

$$(18) \quad A_1 = RT \ln \left(\frac{K_1 A Y}{X P} \right) ,$$

$$(19) \quad A_2 = RT \ln \left(\frac{K_2 A}{X Z^2} \right) ,$$

$$(20) \quad A_3 = RT \ln \left(\frac{K_3 X Y}{P^2} \right) ,$$

$$(21) \quad A_4 = RT \ln \left(\frac{K_4 X^2}{A P} \right) ,$$

$$(22) \quad A_5 = RT \ln \left(\frac{K_5 B Z}{Y} \right) .$$

We need now to evaluate the Onsager tensor at equilibrium. It is obtained by expressing the fluxes (12), (13) and (14) in terms of the forces (15), (16) and (17) and by linearizing such that

$$(23) \quad v_i = L_{ij} F^j .$$

A tedious but straightforward computation gives

$$(24) \quad L_{11} = \sqrt{\frac{Pk}{k_4}} \left(4A\sqrt{Pk k_4} + \sqrt{k k_4} P^{3/2} + k_2 A^{3/2} + \sqrt{A P k} \right) ,$$

$$L_{12} = L_{21} = \sqrt{\frac{Pk}{k_4}} \left(\sqrt{k k_4} P^{3/2} - \sqrt{A P k} \right) ,$$

$$L_{13} = L_{31} = 2\sqrt{\frac{Pk}{k_4}} A^{3/2} k_2 ,$$

$$L_{22} = \frac{k P^{3/2}}{k_1 \sqrt{k_4 A}} \left(A k_1 \sqrt{k} + k^{3/2} + k_1 \sqrt{P A k_4} \right) ,$$

$$L_{23} = L_{32} = -\frac{k^{5/2} P^{3/2}}{\sqrt{A k_4 k_1}} ,$$

$$L_{33} = \frac{\sqrt{P k} (4A^2 k_1 k_2 + k^2 P)}{k_1 \sqrt{k_4 A}} .$$

The last step is to evaluate the metric tensor $g_{\mu\nu}$ corresponding to the chemical system such that

$$(25) \quad v_\mu = g_{\mu\nu} F^\nu$$

and such that $g_{\mu\nu}$ reduces to L_{ij} at equilibrium.

The metric can be evaluated from the known value of the fluxes in terms of the forces (eqs. (12)-(14)) and after some algebraic manipulations we obtain

$$(26) \quad \begin{aligned} g_{11}F^1 &= 2APk(1 - e^{2F^1}) - \frac{k_3P^2k^2}{k_1k_4} \left(e^{-F^1-F^2} + 1 - e^{-F^2} \right) + \\ &\quad + P^2k + \sqrt{\frac{Pk}{k_4}} k_2 A^{3/2} \left(e^{-F^1} - e^{-2F^1-2F^3} + e^{-2F^3} - 1 \right) - \\ &\quad - P^{3/2}k^{3/2} \sqrt{\frac{A}{k_4}} \left(e^{-F^1} - 1 \right), \\ g_{12}F^2 &= -\frac{k_3P^2k^2}{k_1k_4} \left(e^{-F^2} - 1 \right) + P^{3/2}k^{3/2} \sqrt{\frac{A}{k_4}} \left(e^{-F^2} - 1 \right), \\ g_{13}F^3 &= k_2 A^{3/2} \sqrt{\frac{Pk}{k_4}} \left(1 - e^{-2F^3} \right), \\ g_{21}F^1 &= \sqrt{\frac{A}{k_4}} P^{3/2}k^{3/2} \left(e^{-F^1} - 1 \right) - \frac{k_3P^2k^2}{k_1k_4} \left(e^{-F^1} - 1 \right), \\ g_{22}F^2 &= \frac{k_3P^2k^2}{k_1k_4} \left(e^{-F^1} - 1 - e^{-F^1-F^2} \right) + kP^2 - \sqrt{\frac{A}{k_4}} P^{3/2}k^{3/2} \left(e^{-F^2} - 1 \right) - \\ &\quad - \frac{k^{5/2}P^{3/2}}{k_1\sqrt{Ak_4}} e^{-F^2} + \frac{k_5k_4^{1/4}A^{1/4}B\sqrt{k_2}}{k^{3/4}P^{1/4}}, \\ g_{23}F^3 &= \frac{k_5k_4^{1/4}A^{1/4}B\sqrt{k_2}}{k^{3/4}P^{1/4}} \left(e^{-F^3} - 1 \right), \\ g_{31}F^1 &= 2\sqrt{\frac{Pk}{k_4}} A^{3/2}k_2 \left(1 - e^{-F^1} \right), \\ g_{32}F^2 &= \frac{k^{5/2}P^{3/2}}{k_1\sqrt{Ak_4}} \left(e^{-F^2} - 1 \right), \\ g_{33}F^3 &= 2\sqrt{\frac{kP}{k_4}} A^{3/2}k_2 \left(2e^{-F^1} - e^{-2F^1-2F^3} - 1 \right) - \\ &\quad - \frac{k_4^{1/4}A^{1/4}k_5B\sqrt{k_2}}{k^{3/4}P^{1/4}} e^{-F^3} + \frac{k^{5/2}P^{3/2}}{k_1\sqrt{Ak_4}} \left(e^{-F^2} - 1 \right). \end{aligned}$$

As known, the metric tensor is symmetric near equilibrium. Moreover, far from equilibrium, in particular when the thermodynamic system reaches a bifurcation point, the metric tensor will lose its symmetric property showing also the skew-symmetric part. To test this statement, we have numerically solved the chemical kinetic (eq. (4)) starting

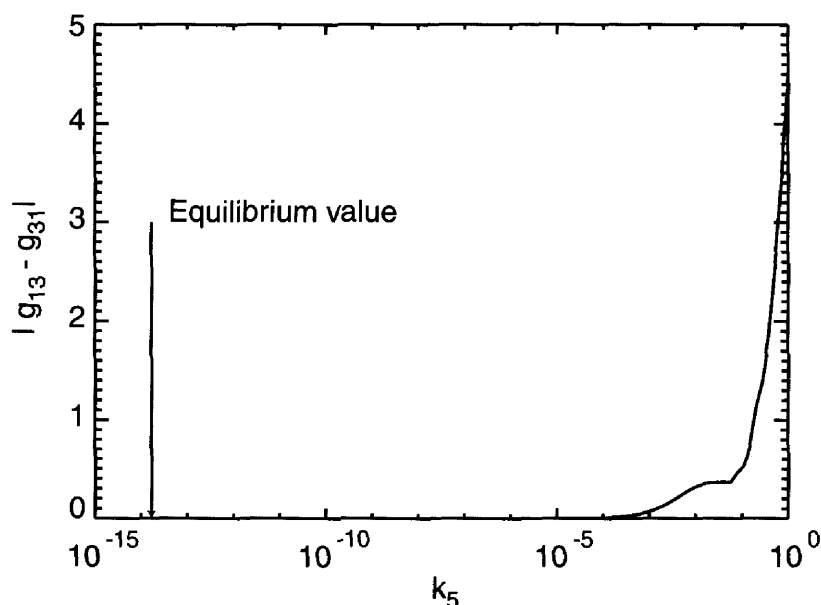


Fig. 3. – Absolute difference between transposed metric components with respect to the distance from equilibrium (denoted by the arrow). The control parameter, k_5 , is in logarithmic scale. The difference vanishes at equilibrium (according to Onsager's theory) and strongly increases when the system reaches its oscillatory state. For k_5 close to unity, the system has reached a stable limit cycle.

from the equilibrium state and changing one of the parameters in order to drive the system away from equilibrium to its oscillatory state.

Figure 3 displays the absolute difference between transposed component of the metric tensor $|g_{\mu\nu} - g_{\nu\mu}|$ as we move away from the equilibrium state marked by an arrow.

4. – Conclusion

According to our theory (ref. [1]) we have verified, using a simple chemical example, the existence of the skew-symmetric part of the metric tensor when a thermodynamic system is far from equilibrium. We have chosen to explore this kind of model because, as known, a chemical system exhibits rapidly the non-linear relations between affinities and chemical velocities.

The method we used to construct the metric tensor of the chemical model can be followed in general. It takes into account Onsager's theory, when the system is near equilibrium, and gives a suitable definition of the thermodynamic variables which allow the entropy production to be expressed as a sum of products of forces and their conjugated fluxes.

The mathematical complexity of the theory raises problems to explore analytically more complex systems. Moreover, complex systems have to be analyzed numerically and experimentally to test the validity of the theory. At present, we are investigating non-linear effects foreseen by the theory in the Hall systems.

REFERENCES

- [1] SONNINO G., this issue, p. 1057.
- [2] GLANSDORFF P. and I. PRIGOGINE, *Structure, Stabilité et Fluctuations* (Masson, Paris) 1971.
- [3] PRIGOGINE I. and R. LEFEVER, *J. Chem. Phys.*, **48** (1968) 1695.
- [4] KONDEPUDI D. and I. PRIGOGINE, *Modern Thermodynamics, From Heat Engines to Dissipative Structures* (John Wiley, New York) 1998.
- [5] HAASE R., *Thermodynamics of Irreversible Processes* (Dover, New York) 1969.
- [6] PRIGOGINE I., *Introduction to Thermodynamics of Irreversible Processes* (John Wiley, New York) 1962.