Thermodynamic field theory: Chemical examples(*)

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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.

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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.

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

\[(h_{\mu\nu})^0_{i,\rho} = 0.\]

The approximated solution of eq. (1) is

\[h_{\mu\nu} \approx \hat{L}_{\mu\nu} \frac{1 - e^{-(\Gamma_3 \hat{X}^2 + \hat{X}^1)}}{\Gamma_3 \hat{X}^2 + \hat{X}^1} - L_{\mu\nu}, \quad \text{if} \quad \frac{\hat{X}^2}{\sqrt{\Gamma^{22}}} < \frac{\hat{X}^1}{\sqrt{\Gamma^{11}}},\]

\[h_{\mu\nu} \approx \hat{L}_{\mu\nu} \frac{1 - e^{-(\Gamma_1 \hat{X}^1 + \hat{X}^2)}}{\Gamma_1 \hat{X}^1 + \hat{X}^2} - L_{\mu\nu}, \quad \text{if} \quad \frac{\hat{X}^2}{\sqrt{\Gamma^{22}}} > \frac{\hat{X}^1}{\sqrt{\Gamma^{11}}},\]

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 \(\hat{X}^\mu = X^\mu/R\) (\(X^\mu\) 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 D donner (see also fig. 1)

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

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:

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A + Y \rightleftharpoons X + P$</td>
<td>$\omega_1 = k_1AY - kXP$</td>
</tr>
<tr>
<td>$A + Y \rightleftharpoons 2X + 2Z$</td>
<td>$\omega_2 = k_2AX - kX^2Z^2$</td>
</tr>
<tr>
<td>$X + Y \rightleftharpoons 2P$</td>
<td>$\omega_3 = k_3XY - kP^2$</td>
</tr>
<tr>
<td>$2X \rightleftharpoons A + P$</td>
<td>$\omega_4 = k_4X^2 - kAP$</td>
</tr>
<tr>
<td>$B + Z \rightleftharpoons \frac{f}{2}Y$</td>
<td>$\omega_5 = k_5BZ - kY^{1/2}$</td>
</tr>
</tbody>
</table>

(4)

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) 
\[
k = \frac{k_1k_A}{k_3},
\]

(6) 
\[
P^{7/2} = K_1^2K_2K_4^{3/2}K_5^{2}B^2,
\]

(7) 
\[
X_{eq}^2 = \frac{kAP}{k_4},
\]

(8) 
\[
Y_{eq} = k\sqrt{\frac{APk}{k_4}} \frac{P}{k_1A},
\]

(9) 
\[
Z_{eq} = \frac{k^2P}{k_1k_5B} \sqrt{\frac{Pk}{Ak_4}},
\]

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

$$A_l = \sum_{r=1}^{R} b_{rl} F_r,$$

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

$$v_r = \sum_{l=1}^{L} b_{rl} \omega_l.$$

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

$$v_1 = \omega_1 + \omega_2 - \omega_3 - 2\omega_4,$$
(13) \[ v_2 = -\omega_1 - \omega_3 + \omega_5, \]
(14) \[ v_3 = 2\omega_2 - \omega_5. \]

and, then

(15) \[ F^1 = -\frac{1}{2} \frac{A_4}{RT}, \]
(16) \[ F^2 = -\frac{1}{2} \frac{A_4}{RT} - \frac{A_1}{RT}, \]
(17) \[ F^3 = \frac{1}{2} \frac{A_2}{RT} + \frac{1}{4} \frac{A_4}{RT}, \]

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

(18) \[ A_1 = RT \ln \left( \frac{K_1AY}{XP} \right), \]
(19) \[ A_2 = RT \ln \left( \frac{K_2A}{XZ^2} \right), \]
(20) \[ A_3 = RT \ln \left( \frac{K_3XY}{P^2} \right), \]
(21) \[ A_4 = RT \ln \left( \frac{K_4X^2}{AP} \right), \]
(22) \[ A_5 = RT \ln \left( \frac{K_6BZ}{Y} \right). \]

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) \[ v_i = L_{ij} F^j. \]

A tedious but straightforward computation gives

(24) \[ L_{11} = \sqrt{\frac{P^k}{k_4}} \left( 4A\sqrt{Pkk_4} + \sqrt{kk_4P^{3/2} + k_2A^{3/2}} + \sqrt{APk} \right), \]

\[ L_{12} = L_{21} = \sqrt{\frac{P^k}{k_4}} \left( \sqrt{kk_4P^{3/2} - \sqrt{APk}} \right), \]

\[ L_{13} = L_{31} = 2\sqrt{\frac{P^k}{k_4}} A^{3/2}k_2, \]

\[ L_{22} = \frac{kP^{3/2}}{k_1\sqrt{Ak_4}} \left( Ak_1\sqrt{k} + k^{3/2} + k_1\sqrt{PAk_4} \right), \]

\[ L_{23} = L_{32} = -\frac{k^{5/2}P^{3/2}}{\sqrt{Ak_4k_1}}, \]

\[ L_{33} = \frac{\sqrt{P^k}(4A^2k_1k_2 + k^2P)}{k_1\sqrt{Ak_4}}. \]
The last step is to evaluate the metric tensor $g_{\mu\nu}$ corresponding to the chemical system such that

\[ v_\mu = g_{\mu\nu} F^\nu \]

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

\[
\begin{align*}
g_{11} F^1 &= 2APk(1 - e^{2F^1}) - \frac{k_3 P^2 k^2}{k_1 k_4} \left( e^{-F^1-F^2} + 1 - e^{-F^2} \right) + \\
&\quad + P^2 k + \sqrt{\frac{P k}{k_4}} k_2 A^{3/2} \left( e^{-F^1} - e^{-2F^1-2F^3} + e^{-2F^3} - 1 \right) - \\
&\quad - P^{3/2} k^{3/2} \sqrt{\frac{A}{k_4}} (e^{-F^1} - 1) , \\
g_{12} F^2 &= -\frac{k_3 P^2 k^2}{k_1 k_4} (e^{-F^2} - 1) + P^{3/2} k^{3/2} \sqrt{\frac{A}{k_4}} (e^{-F^2} - 1) , \\
g_{13} F^3 &= \frac{k_2 A^{3/2}}{k_4} \sqrt{\frac{Pk}{k_4}} (1 - e^{-2F^3}) , \\
g_{21} F^1 &= \sqrt{\frac{A}{k_4}} P^{3/2} k^{3/2} \left( e^{-F^1} - 1 \right) - \frac{k_3 P^2 k^2}{k_1 k_4} (e^{-F^1} - 1) , \\
g_{22} F^2 &= \frac{k_3 P^2 k^2}{k_1 k_4} \left( e^{-F^1} - 1 - e^{-F^1-F^4} \right) + kP^2 - \sqrt{\frac{A}{k_4}} P^{3/2} k^{3/2} (e^{-F^2} - 1) - \\
&\quad - \frac{k^{5/2} P^{3/2}}{k_1 A k_4} e^{-F^2} + \frac{k_5 k_4^{1/4} A^{1/4} B \sqrt{k_2}}{k^{3/4} P^{1/4}} , \\
g_{23} F^3 &= \frac{k_5 k_4^{1/4} A^{1/4} B \sqrt{k_2}}{k^{3/4} P^{1/4}} (e^{-F^3} - 1) , \\
g_{31} F^1 &= 2 \sqrt{\frac{Pk}{k_4}} A^{3/2} k_2 (1 - e^{-F^1}) , \\
g_{32} F^2 &= \frac{k^{5/2} P^{3/2}}{k_1 A k_4} (e^{-F^2} - 1) , \\
g_{33} F^3 &= 2 \sqrt{\frac{kP}{k_4}} A^{3/2} k_2 \left( 2e^{-F^1} - e^{-2F^1-2F^3} - 1 \right) - \\
&\quad - \frac{k_4^{1/4} A^{1/4} k_5 B \sqrt{k_2}}{k^{3/4} P^{1/4}} e^{-F^3} + \frac{k_5^{5/2} P^{3/2}}{k_1 A k_4} (e^{-F^2} - 1) .
\end{align*}
\]

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
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 $|g_{ij} - g_{ji}|$ 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