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TOPOLOGICAL METHODS IN CHEMICAL KINETICS

ON THE APPLICABILITY OF THERMODYNAMICS TO MASS ACTION KINETICS

B. Milicevic
Scientific Computation Centre
CIBA-GEIGY Ltd., Basle, Switzerland

SUMMARY

After a short introduction to the needed equilibrium thermodynamics formulated on dual linear vector spaces, a corresponding approach to nonequilibrium thermodynamics of a specific class of gradient dynamical systems is developed. Illustrative examples from formal mass action kinetics are then discussed to demonstrate the narrowness of the applicability range of thermodynamics to dynamical systems of interacting species. The whole treatment is restricted to the well known qualitative topological methods, used also for mathematical modeling of chemical and biological processes.

I. INTRODUCTION

In the many different approaches to thermodynamics, as far as is known to the author, the first attempt to use vector analysis in thermodynamics has been made by Kobozev [1], presumably motivated by the ideas of Bridgman [2]. Some time later Milicevic [3] published an approach to chemical thermodynamics based on gradient vector fields and scalar products. Developing the nonlinear thermodynamics Glansdorff and Prigogine [4] and Nicolis [5] used scalar and vector potentials as fundamental concepts for the establishment of the evolution criterion. A formulation of thermodynamics founded on the properties of the Hilbert space was recently developed by Weinhold [6]. Although all mentioned authors have obviously done their work independently, many similar ideas can be detected in all this work. The treatments [3] and [6], inspired by the recognition of Tisza [7] that in the Gibbs space no physically meaningful metric is definable, will be used here as the starting point.

After a short introduction to that formalism, in this paper the application of thermodynamics to dynamical systems of interacting species in the sense of Andronov et al. [8, 9] is given. Selected examples from mass action kinetics are then treated mostly by topological methods and their physical meaning is discussed.

The whole approach is oriented to an as simple as possible presentation of fundamental ideas and therefore no generalisations are made. Closed and open isothermal isobaric systems only are considered. The appropriate thermodynamic energy function is the Gibbs function G^*, which has been uniquely defined by Tisza [10] and Callen [11] as a Legendre transform of the internal energy of the system.

II. OUTLINES OF THE BASIC FORMALISM

Using an isothermal isobaric homogeneous three-component system as a demonstration example the main results from [3] and [6] relevant to the matter discussed here, will be now given.

The content of the system can be expressed by moles m_i of present species in the volume. In closed systems it is convenient to replace them by dimensionless mole fractions x_i and to use the expression:

$$\sum_{i=1} x_i = 1 \tag{1}$$

These quantities are derived from measurement and can therefore be treated as real numbers.

Because

$$x_i \geq 0 \tag{2}$$

the composition of the system will be given in the appropriate Euclidean space:

$$\mathbb{R}^3 = \{\underline{\tilde{x}}: x_1, x_2, x_3\} \tag{3}$$

by the row vector $\underline{\tilde{x}}$ in the positive orthant. The space norm inducing metric ($\underline{x}$: column vector):

$$|\underline{x}| = \sqrt{\langle \underline{\tilde{x}} | \underline{x} \rangle} \tag{4}$$

follows from the existence of the scalar product $\langle \cdot | \cdot \rangle$.

The sole necessary assumption to describe the here treated thermodynamics is, that there exists a C^2-scalar function

$$G(\underline{\tilde{x}}) = G^*/R^*T^* \tag{5}$$

(R^*: gas constant, T^*: temperature) which in the positive orthant of the considered space has all properties of the dimensionless Gibbs function.

For this purpose consider the neighbourhood $N \subset W$ of a particular point $\underline{\tilde{x}}_s \in W$ and define on the open set $W \subset \mathbb{R}^3$:

$$\underline{\tilde{g}} = \text{grad } G(\underline{\tilde{x}}) \tag{6}$$

where $G: N \to \mathbb{R}$

and $\quad \text{grad } G: N \to \mathbb{R}^3$

represents the corresponding conservative force field. In the positive orthant the vector $\tilde{\underline{g}}$ can be now uniquely identified as the chemical potential vector.

For the rotation of this gradient vector field

$$\text{curl } \underline{g}: \mathbb{R}^3 \to \mathbb{R}^3$$

as is well known, results

$$\text{curl grad } G(\underline{x}) = \begin{bmatrix} 0 & -\frac{\partial}{\partial x_3} & \frac{\partial}{\partial x_2} \\ \frac{\partial}{\partial x_3} & 0 & -\frac{\partial}{\partial x_1} \\ -\frac{\partial}{\partial x_2} & \frac{\partial}{\partial x_1} & 0 \end{bmatrix} \begin{bmatrix} g_1 \\ g_2 \\ g_3 \end{bmatrix} = \underline{0} \qquad (7)$$

respectively

$$\frac{\partial g_i}{\partial x_j} = \frac{\partial g_j}{\partial x_i} \qquad (8)$$

The relations (8) express exactly the first law of thermodynamics in terms of the Gibbs energy function $G(\underline{x})$.

Note additionally, that on an arbitrary nonconservative vector field, using the Helmholtz theorem [12], a vector point function $\underline{h}(\underline{x})$ with a lamelar and a solenoidal part can be defined

$$\underline{h}(\underline{x}) = -\text{ grad } L(\underline{x}) + \text{curl } \underline{s}(\underline{x}) \qquad (9)$$

which implies as well known

$$\text{curl grad } L(\underline{x}) = \underline{0}\ , \quad \text{div curl } \underline{s}(\underline{x}) = 0$$

This very interesting topic is treated in more detail by Glansdorff and Prigogine [4] and Nicolis [5]. The existence of a vector potential such as (9) violates however the first law of thermodynamics and will be considered only briefly here.

Proceeding further, it follows that the scalar products:

$$G = \langle \tilde{\underline{g}} | \underline{x} \rangle \tag{11}$$

$$0 = \langle \tilde{\underline{x}} | d\underline{g} \rangle \tag{12}$$

$$dG = \langle \tilde{\underline{g}} | d\underline{x} \rangle \tag{13}$$

are very well known thermodynamic expression for $\underline{g}$. The Gibbs function of a mixture is given by (11). The Gibbs-Duhem relation is expressed with the bilinear form (12). The condition that (13) is an exact differential ($dG = 0$) states the second law of thermodynamics, i.e. that in equilibrium

$$g_1 = g_2 = g_3 \tag{14}$$

must hold.

III.

TERMINOLOGICAL REMARKS

In the following text several planar (: two-component) dynamical systems of interacting species will be considered. Singularity points $\underline{x}_s$ in the phase plane [8] play thereby a dominante role. The terminology used in literature for this purpose is partially very different (c.f. Table I). To avoid confusion, the terminology used here for singularity points is defined in Fig. 1.

Table I: Different terminology for singularity points

<table>
<tr><th>This work</th><th>Ref. [8, 9]</th><th>Ref. [13]</th><th>Ref. [14]</th><th>Ref. [15]</th></tr>
<tr><td>Degenerate node</td><td>Multiple point</td><td>--</td><td>--</td><td>--</td></tr>
<tr><td rowspan="2">Improper node</td><td rowspan="3">Node</td><td>Focus</td><td rowspan="2">Proper or improper node</td><td>Star</td></tr>
<tr><td>Improper node</td><td rowspan="2">Node</td></tr>
<tr><td>Node</td><td>Node</td><td>Improper node</td></tr>
<tr><td>Focus</td><td>Focus</td><td>Spiral</td><td>Spiral</td><td>Focus</td></tr>
<tr><td>Centre</td><td>Centre</td><td>Centre</td><td>Centre</td><td>Vortex</td></tr>
<tr><td>Saddle</td><td>Saddle</td><td>Saddle</td><td>Saddle</td><td>Saddle</td></tr>
</table>

Note that, if the planar (linear or linearized) dynamical system (with the origin of coordinates transferred in the singularity point) is given by the autonomous system of ordinary differential equations

$$\dot{\underline{y}} = \underline{\underline{B}}\ \underline{y} \qquad (15)$$

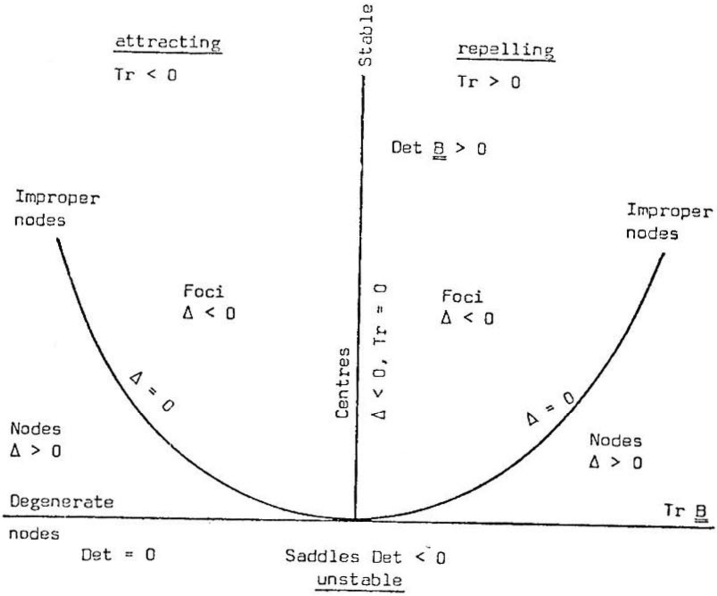
($\dot{\underline{y}}$: dimensionless time derivative), then with the trace (Tr) and determinant (Det) of the Jacobian matrix evaluated at $\underline{y} = \underline{0}$, the characteristic polynomial for the eigenvalues λ is:

$$\lambda^2 - (\mathrm{Tr}\ \underline{\underline{B}})\ \lambda + \mathrm{Det}\ \underline{\underline{B}} = 0 \qquad (16)$$

The corresponding discriminant is defined as

$$\Delta = (\mathrm{Tr}\ \underline{\underline{B}})^2 - 4\ \mathrm{Det}\ \underline{\underline{B}} \qquad (17)$$

Fig. 1: Stability diagram for singularity points



IV.

GRADIENT DYNAMICAL SYSTEMS

The kinetics of particular chemically reacting systems was investigated by Gavalas [16] using the theory of manifolds. Here only the derived formulae from section II. will be applied to gradient dynamical systems such as discussed by Hirsch and Smale [13].

The existence and uniqueness of the solutions for the considered initial value problems [15] are assumed to be given. Because of (2) the trajectories of integral curves have only a physical meaning if they are bounded in the positive orthant of $\mathbb{R}^2$, which now represents the phase plane [8] of the dynamical systems investigated.

To establish the applicability of the Gibbs function to such nonequilibrium systems two points are considered:

i. The validity of the first law of thermodynamics

ii. The existence of G as a Liapunov function [17], which implies the validity of the second law of thermodynamics.

Taking now the dimensionless time derivative of (13) in appropriately changed coordinates

$$\dot{G}(\underline{y}) = \langle \underline{\tilde{g}} | \underline{\dot{y}} \rangle \tag{18}$$

it is obvious that the two mentioned points will strongly depend on the properties of the matrix $\underline{\underline{B}}$ from (15).

For the particular gradient dynamical system

$$\underline{\dot{y}} = - \operatorname{grad} G(\underline{y}) \tag{19}$$

where $G: N \rightarrow \mathbb{R}$ ist a C^2-function, it is easy to prove, that both points are satisfied.

The corresponding Jacobian matrix for any singularity point $\underline{x}_s \in W$ of (15)

$$\underline{\underline{B}} = - \begin{bmatrix} \frac{\partial g_1}{\partial y_1} & \frac{\partial g_1}{\partial y_2} \\ \frac{\partial g_2}{\partial y_1} & \frac{\partial g_2}{\partial y_2} \end{bmatrix} \tag{20}$$

is symmetric, which reflects the validity of the first law of thermodynamics. The equations (15) represent therefore the known equations of irreversible thermodynamics [18] and the symmetry property of $\underline{\underline{B}}$ expresses the celebrated Onsager relationship.

From (18) and (19) it follows

$$\dot{G}(\underline{y}) = - |\underline{g}|^2 \leq 0 \tag{21}$$

i.e. if additionally $G(\underline{y}) > 0$ and $G(\underline{0}) = 0$ hold, G will be a Liapunov function.

The symmetry property of the matrix $\underline{\underline{B}}$ leads to the necessary but not sufficient condition [13], that $G(\underline{y})$ can be only a Liapunov function when the singularity point is an attracting or a stable degenerate node.

This reasoning is also true for arbitrary defined scalar products and corresponding gradient fields, e.g. from the Thom catastrophe Theory [19], where, however, the physical meaning of $G(\underline{y})$ can be completely lost.

With the selected examples from mass action kinetics it will be shown, that in simplest cases often the symmetry of $\underline{\underline{B}}$ is not given and under the variety of appropriate Liapunov functions one such as $G(\underline{y})$ must not exist, as pointed out firstly by Wei [20].

V.

SELECTED ILLUSTRATIVE EXAMPLES

All examples are taken from the classical mass action kinetics. No generalisations e.g. of Horn and Jackson [21] or of Oster and Perelson [22] are discussed.

For the model reaction diagrams the flow graphs of Clarke [23] are used. The different species are designated by X_i, the flows by arrows (the barbs and feathers defining the interaction stochiometry), the rate constants by $k_i > 0$.

1. Stable degenerate node

The scheme

$$X_1 \xrightarrow{k_1} X_2$$

represents the simplest model for a closed system of two interacting species. Introducing the dimensionless time $\tau = k_1 t$ and using mole fractions for the mass balance

$$x_2 = 1 - x_1 \tag{22}$$

it follows for the singularity point ($\dot{\underline{x}} = \underline{0}$): $x_{1s} = 0$, $x_{2s} = 1$. The corresponding singular matrix

$$\underline{\underline{B}} = \begin{bmatrix} -1 & 0 \\ 1 & 0 \end{bmatrix}$$

yields: Tr $\underline{\underline{B}} = -1$, Det $\underline{\underline{B}} = 0$, $\Delta = 1$. Therefore the point is a non-repelling degenerate node. The matrix $\underline{\underline{B}}$ is nonsymmetric i.e. the first law of thermodynamics is violated and therewise $G(\underline{y})$ as a Liapunov function is not physically meaningful. Taking, however

$$V(\underline{y}) = \frac{1}{2} y_1^2 + \frac{1}{2} y_2^2$$

and making use of (22), it results

$$\dot{V}(\underline{y}) = - y_1^2 - y_1^2 < 0$$

The degenerate node is in sense of Liapunov attracting. For arbitrary initial conditions the composision of the system will be given by (22) in the phase plane.

2. Equilibrium point

Consider now

$$X_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X_2$$

Proceeding as in the previous example it follows

$$x_{1s} = \frac{1}{K + 1}, \quad x_{2s} = \frac{K}{K + 1}, \quad K = \frac{k_1}{k_2} = \frac{x_{2s}}{x_{1s}}$$

The corresponding matrix

$$\underline{\underline{B}} = \begin{bmatrix} -K & 1 \\ K & -1 \end{bmatrix}$$

is again singular and the system will obey the first law of thermodynamics only if

$$K = 1$$

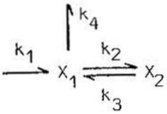
holds. The equilibrium point is an attracting degenerate node:

$$G(\underline{0}) = 0, \quad G(\underline{y}) > 0, \quad \dot{G}(\underline{y}) \leq 0$$

In this case expressions such as "near" and "far" from equilibrium are meaningless. When the system is out of equilibrium the equations (15) and the conditions (18), (19), (20) will be perpetually satisfied.

3. Stationary point

The system



is open and mole fractions can no more be used. Introducing however

$$x_1 = \frac{k_4}{k_1} m_1, \quad x_2 = \frac{k_4}{k_1} m_2, \quad \tau = k_4 t, \quad a = \frac{k_2}{k_4}, \quad b = \frac{k_3}{k_4}$$

the dimensionless equations result

$$\dot{x}_1 = 1 - (a+1)\,x_1 + bx_2$$
$$\dot{x}_2 = ax_1 - bx_2$$

For $\underline{\dot{x}} = 0$, the singularity point has the value $x_{1s} = 1$, $x_{2s} = a/b$, i.e.

$$\frac{x_{2s}}{x_{1s}} = \frac{a}{b} = \frac{k_2}{k_3} = K$$

holds. After transferring the origin of coordinates in the singularity point it is obvious that only for

$$K = 1$$

a symmetric matrix follows:

$$\underline{\underline{B}} = \begin{bmatrix} -(b+1) & b \\ b & -b \end{bmatrix}$$

From

$$\mathrm{Tr}\ \underline{\underline{B}} = -\ (2b+1) < 0$$
$$\mathrm{Det}\ \underline{\underline{B}} = b > 0$$
$$\Delta = 4b^2 + 1 > 0$$

the singularity point can be identified as an attracting node. All trajectories will therefore terminate in this singularity i.e. all flows in the phase plane will asymptotically (: $\tau \to \infty$) reach this stationary point.

Although the considered system for $K = 1$ obeys to the first law of thermodynamics $G(\underline{y})$ is not a Liapunov function for it.

To get an appropriate Liapunov function a similarity transformation [24] often used in the theory of oscillations [25] can be used. The first order system of equations (15) is equivalent to the second order equation

$$\ddot{y}_1 - (\mathrm{Tr}\ \underline{\underline{B}})\ \dot{y}_1 + (\mathrm{Det}\ \underline{\underline{B}})\ y_1 = 0$$

Introduction of a new variable ($\dot{y}_1 = z$) leads to

$$\underline{\underline{D}}^{-1}\ \underline{\underline{B}}\ \underline{\underline{D}} = \begin{bmatrix} 0 & 1 \\ -\ \mathrm{Det}\ \underline{\underline{B}} & \mathrm{Tr}\ \underline{\underline{B}} \end{bmatrix}$$

A Liapunov function can be now easily found (for Det $\underline{\underline{B}} > 0$)

$$V(y_1, \dot{y}_1) = \frac{\mathrm{Det}\ \underline{\underline{B}}}{2}\ y_1^{\,2} + \frac{1}{2}\ \dot{y}_1^{\,2}$$

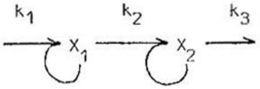
$$\dot{V}(y_1, \dot{y}_1) = \mathrm{Tr}\ \underline{\underline{B}}\ \dot{y}_1^{\,2} = -\ (2b+1)\ \dot{y}_1^{\,2} < 0$$

which in their general form holds also for $K \neq 1$.

Note that this Liapunov function is nonthermodynamic, because the phase plane is changed. From a practical point of view it is interesting to mention, that the behaviour of the two-component system can, in such a phase plane, be described in terms of variables of only one component.

4. Stable closed orbits

The Lotka-Volterra predator-prey model known from numerous publications



will be now discussed briefly with the method used here.

Introduction of the dimensionless quantities

$$x_1 = \frac{k_2}{k_3}\, m_1, \quad x_2 = \frac{k_2}{k_3}\, m_2, \quad \tau = k_3 t, \quad a = \frac{k_1}{k_3}$$

yield the rate equations

$$\dot{x}_1 = ax_1 - x_1x_2$$
$$\dot{x}_2 = - x_2 + x_1x_2$$

Two singularity points exist: $x'_{1s} = 0$, $x'_{2s} = 0$ and $x_{1s} = 1$, $x_{2s} = a$.

For the first singularity the matrix of the linearized system is symmetric and has a determinant with negative sign. The singularity point is therefore an (unstable) saddle and in its neighbourhood the system is conservative.

After transferring the origin in the second singularity and linearizing, the matrix of the equations system reads

$$\underline{\underline{B}} = \begin{bmatrix} 0 & -1 \\ a & 0 \end{bmatrix}$$

This matrix is nonsymmetric, and yields $\text{Tr}\ \underline{\underline{B}} = 0$, $\text{Det}\ \underline{\underline{B}} = a$, $\Delta = - 4a$. Therefore the singularity point is a centre surrounded by closed orbits in its neighbourhood:

$$x_1 x_2{}^a e^{-[(x_1-1)+(x_2-a)]} = \text{const.}$$

Because of the existence of the saddle in the origin of the phase plane these orbits are bounded in the positive orthant of $\mathbb{R}^2$.

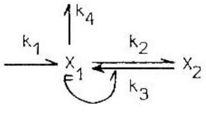
The <u>Liapunov</u> function is given by

$$V(\underline{y}) = \frac{1}{2} y_1{}^2 + \frac{1}{2a} y_2{}^2$$
$$\dot{V}(\underline{y}) = - y_1y_2 + y_1y_2 = 0$$

Therefore no flow can reach the centre i.e. a stable but not attracting stationary point. The system will be either in this point (: state) or oscillate with a constant period.

5. Limit cycle

For the model system



Lefever and Nicolis [26] showed that it can exhibit the behaviour of a limit cycle. Transforming the original rate equations in a second order equation of Liénard type, the authors proved by a theorem of Levinson and Smith [27], the existence of an attracting closed orbit. For the same purpose Poore [28] used the Hopf bifurcation theory [29]. Tyson [30, 31] finally proved that the solutions of the rate equations are bounded in a certain domain of the positive orthant and estimated the boundary of the corresponding open set in $\mathbb{R}^2$.

Here this model will be discussed from a specific point of view.

Introducing as before

$$x_1 = \sqrt{\frac{k_3}{k_4}}\, m_1, \quad x_2 = \sqrt{\frac{k_3}{k_4}}\, m_2, \quad \tau = k_4 t$$

$$a = \frac{k_1}{k_4}\sqrt{\frac{k_3}{k_4}}, \quad b = \frac{k_2}{k_4}$$

the dimensionless rate equations follow

$$\dot{x}_1 = a - (b+1)\, x_1 + x_1{}^2 x_2$$

$$\dot{x}_2 = b x_1 - x_1{}^2 x_2$$

Note that "a" and "b" do not appear anymore as the constant concentrations of species [26], but as the dimensionless products of the rate constants.

There exists only one singularity point: $x_{1s} = a$, $x_{2s} = b/a$. Transferring the origin and linearizing leads to

$$\underline{\underline{B}} = \begin{bmatrix} (b-1) & a^2 \\ -b & -a^2 \end{bmatrix}$$

which is a nonsymmetric matrix for arbitrary values of their elements. Note further:

$$\mathrm{Tr}\ \underline{\underline{B}} = b - a^2 - 1$$

$$\mathrm{Det}\ \underline{\underline{B}} = a^2 > 0$$

$$\Delta = (b - a^2 - 1)^2 - 4a^2$$

Using the same similarity transformation as in example 3, for the Liapunov function in the changed phase plane follows

$$V(y_1,\dot{y}_1) = \frac{\mathrm{Det}\ \underline{\underline{B}}}{2}\ {y_1}^2 + \frac{1}{2}\ {\dot{y}_1}^2$$

$$\dot{V}(y_1,\dot{y}_2) = (\mathrm{Tr}\ \underline{\underline{B}})\ {\dot{y}_1}^2$$

It is obvious that the singularity point will be for Tr $\underline{\underline{B}} < 0$ attracting, for Tr $\underline{\underline{B}} = 0$ stable and for Tr $\underline{\underline{B}} > 0$ repelling. Depending on the sign of Δ it will be a node, a focus or a centre.

As is known the repelling focus(Tr $\underline{\underline{B}} > 0$, $\Delta < 0$) is surrounded by an attracting closed orbit. The existence of this limit cycle can be proved [28] using Hopf bifurcation theory [29].

For the particular system considered, it is necessary only to add:

when the bifurcation point is given by

$${a_c}^2 = b_c - 1$$

then the variations $(a_c + \alpha)$ and $(b_c + \beta)$ must satisfy

$$\alpha < 0,\ \left.\frac{d\ \mathrm{Tr}\ \underline{\underline{B}}\ (\alpha)}{d\alpha}\right|_{\alpha=0} < 0$$

and

$$\beta > 0, \quad \left.\frac{d \, \mathrm{Tr} \, \underline{\underline{B}} \, (\beta)}{d\beta}\right|_{\beta=0} > 0$$

which indeed hold.

This is however not sufficient as a proof that the limit cycle is bounded in the positive orthant of $\mathbb{R}^2$. To achieve that, it is necessary to prove that the scalar product satisfies always

$$< \tilde{\dot{\underline{x}}} | \underline{n} > \; < 0 \quad \text{on} \quad \partial W$$

($\underline{n}$: outward directed normal to the boundary ∂W of the open set $W \subset \mathbb{R}^2$) in the positive orthant of $\mathbb{R}^2$ as has been done in [31].

Note that Othmer [32], Murray [33] and Hastings and Murray [34] have analysed also a three-component system with analogous mainly topological methods.

VI.

CONCLUSIONS

i. For a specific class of isothermal-isobaric dynamical gradient systems the classical thermodynamic Gibbs function can be used as a physically well defined Liapunov function.

ii. Selected examples from mass action kinetics demonstrate, that the use of classical thermodynamics for description of dynamical systems of interacting species is limited to a very narrow range.

iii. The qualitative mathematical formalism for treatment of "nonthermodynamic" kinetic systems is very powerful, but the interpretation of the results still cannot be given within the frames of an existing physical theory.

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