A Riemannian geometry for thermodynamic state space

Petr Kůrka
Department of Philosophy of Mathematics and Physics,
Faculty of Mathematics and Physics, Charles University
Malostranské náměstí 25, 118 00 Praha 1, Czechoslovakia

Abstract

We consider a class of thermodynamic systems, in which the dynamics of the spontaneous approach to equilibrium is governed by the gradient of negentropy, where the gradient is taken with respect to a Riemannian metric. In open systems (dissipative structures) this gradient field is superposed with a vector field of interactions with environment. We consider three characteristics of the "economy" of dissipative structures: negentropy inflow (income), negentropy consumption (i.e. entropy production), and negentropy surplus (reserves). We derive explicit formulas for these characteristics and for the relations between them.

1 Introduction

The conceptual foundations of thermodynamics have been clarified in the last thirty years by a number of authors (see e.g. [2, 8, 9, 10]). A fundamental concept of any thermodynamic theory is the state space, on which thermodynamic variables are defined. Thermodynamic processes are paths in the state space, while work and heat are functionals acting on processes, usually via integration of differential forms. Thermodynamic theories introduce constraints on possible processes, for example Clausius-Duhem inequality.

For the theory of dissipative structures, which are open thermodynamic systems far from equilibrium (see [4]), it seems desirable to inquire into the structure of processes in more detail. Thus the spontaneous process of the approach to equilibrium should be distinguished form that forced by the flows from environment. For example the entropy production is a property of the former, while the entropy flow is a property of the latter. Both these processes require a theory. Spontaneous thermodynamic processes possess Ljapunov functions, e.g. entropy or another thermodynamic potential. A wide class of dynamical systems possessing Ljapunov functions are gradient systems, so it is tempting to postulate, that the thermodynamic vector field is the gradient field of entropy. However, the simplest thermodynamic systems show, that the dynamics of spontaneous processes cannot be determined by the entropy alone. For example diffusion or rate constants are not derivable from it. Rather, they are geometric properties of the state space.

Nevertheless, gradient is a metric concept, and besides Euclidean metric there are many Riemannian metrics, which yield other gradients. This is the idea behind Shahshahani metric in population genetics: The selection vector field is the negative gradient of fitness function with respect to Shahshahani metric (see [1]). It seems that noneuclidean metrics may be workable for some thermodynamic processes too. Thus we recognize in entropy the basic driving force behind the spontaneous approach to equilibrium. This force, however, is canalized by the geometry of the state space.

From another point of view, we can arrive to the same standpoint by a generalization of linear nonequilibrium thermodynamics. We postulate, that the thermodynamic fluxes are determined from the thermodynamic forces via a positive definite matrix of phenomenological coefficients, but we assume that these coefficients are state dependent. There is also a formal analogy with classical mechanics. While a Hamiltonian vector field is obtained from the energy function and symplectic geometry, a thermodynamic vector field is obtained from the entropy function and Riemannian geometry.

In the present paper we develop this approach in abstract setting. We adopt the approach of [2], which recognizes the prime importance of entropy. Because of formal reasons, however, we use instead negentropy (negative entropy) introduced by Schrdinger in [7]. All thermodynamic data might be encoded in the negentropy function, which is an extensive, convex function of extensive and conservative variables like energy, volume and quantities of components. These extensive variables form the state space (compare with [9]). The intensive variables like temperature or pressure may be obtained through differentiation of negentropy or by taking ratio of extensive variables. Thus energy has no privileged position. It is only one of the variables defining the state space.

We add to this structure a space of (spontaneous) processes, and for each state a positive definite bilinear form, which determines the rates of processes in the current state. The processes lift the form to a positive semidefinite bilinear form on the state space, which in turn determines a Riemannian metric on some of its subspaces. The negative gradient of negentropy with respect to this metric is then the vector field of closed system. In an open system we adjoin a vector field of interactions with environment. This field is subjected to condition that the resulting vector field conserves some intensive variables.

While this approach of gradient field is not completely general (for example negentropy is required to be differentiable, which excludes phase transitions), it seems to work in chemical kinetics, which is the proper domain of dissipative structures. We obtain in this way the mass action law with conservation laws as linear constraints. This conforms with the treatment of chemical kinetics in

[10] and [3]. However, since we consider the flows from environment explicitly, we restrict ourselves to the detailed balanced systems.

This approach enables us to investigate the "economy" of dissipative structures. This is based on the Schrdinger's insight, later worked out by the Brusel School of I.Prigogine, that it is the negentropy, what the living organisms (and dissipative structures) feed on. Thus negentropy is regarded as a value, which is consumed in all nonequilibrium processes. Negentropy consumption (entropy production) expresses the cost of these processes, and it is always nonnegative. The negentropy consumption is balanced by negentropy inflow from environment. This is the income of a dissipative structure. The negentropy available for consumption is the negentropy surplus - the reserves. It is the amount of entropy produced, were the system closed and allowed to attain equilibrium.

2 Closed thermodynamic systems

Recall that a set K is convex, if for any $x, y \in K$ and $0 < a < 1$ there is $ax + (1-a)y \in K$. It is a cone, if for any $x \in K$ and $a > 0$ we have $ax \in K$. A function $S : K \to R_1$ is convex, if $S(ax + (1-a)y) \leq aS(x) + (1-a)S(y)$. It is strictly convex, if this inequality is sharp for any different $x, y \in K$. A function S with positive definite second differential d^2S is strictly convex. S is extensive, if for any $a > 0$ there is $S(ax) = aS(x)$. It is intensive if $S(ax) = S(x)$. If V is a vector space, we denote by V^* the dual vector of its linear forms. A symmetric bilinear form $\omega : V \times V \to R_1$ on a vector space V is positive semidefinite, if $\omega(u, u) \geq 0$ for any vector $u \in V$. It is positive definite if this inequality is sharp for any nonzero $u \in V$.

Definition 1. A closed thermodynamic system (K, S, λ, ν) consists of a state space K, negentropy function S, a process form λ, and a process map ν, subject to following conditions:
1. $K \subseteq R_n$ is an open convex cone.
2. $\nu : R_m \to R_n$ is a linear mapping.
3. For each $x \in K$, $\lambda(x) : R_m^* \to R_m$ is an isomorphism, such that $\lambda^\#(x) : R_m^* \times R_m^* \to R_1$ defined by $\lambda^\#(x)(u, v) = u(\lambda(x)(v))$ is a symmetric, positive definite bilinear form. Moreover, λ depends differentiably on x.
4. $S : K \to R_1$ is an extensive, convex and differentiable function. Moreover, for each $x \in K$, $d^2S(x)$ is positive definite on $Im(\nu) \subseteq R_n$.
5. $Im(\nu) \cap \overline{K} = \{0\}$. (Here $\overline{K}$ is the topological closure.)
6. $x \in \partial K$ & $u \in Im(\nu)$ & $x + u \in K \Rightarrow \lim_{y \to x} dS(y)(u) < 0$. (Here ∂K is the topological boundary.)

Definition 2. We call $L(x) = \nu \circ \lambda(x) \circ \nu^* : R_n^* \to R_n$ the phenomenological form and $F(x) = -L(x)(dS(x)) \in R_n$ the (closed) thermodynamic vector field.

In coordinates $\lambda(x)$ is given by a positive definite symmetric matrix $(\lambda(x)^{ij})_{i,j=1,\ldots,m}$ and ν by matrix $(\nu^i_j)_{i=1,\ldots,n,j=1,\ldots,m}$. Then

$$L^{ik}(x) = \sum_{j,l} \nu^i_j \nu^k_l \lambda^{jl}(x), \quad \frac{dx_i}{dt} = F^i(x) = -\sum_j \frac{\partial S}{\partial x^j} L^{ji}(x)$$

Thus the j-th row ν_j of ν is the direction of the j-th process in K. The vector field F is a linear combination of ν_j with coefficients determined by $\lambda(x)$ and $dS(x)$. Because of condition 5 the vectors ν_j do not span the whole R_n. There are always some linear constraints on the processes. The linearity of these constraints means that they are conservative ($F(u+v) = F(u) + F(v)$) and extensive. Condition 6 says that in the neighbourhood of ∂K the negentropy decreases in directions inside K.

Example 1: Ideal gas. This is a rather trivial example with no processes. Let the state space $K = \{(E,V,N)|E,V,N > 0\}$ be given by energy, volume and number of molecules. Then

$$S(E,V,N) = kN(\frac{5}{2}\ln N - \ln V - \frac{3}{2}\ln E + c)$$

where c is a constant. Let $m = 0$ so that $\nu : \{0\} \to R_3$, $\lambda(x)$ are zero mappings. It is easy to see that (K, S, ν, λ) is a closed thermodynamic system. Since $Im(\nu) = \{0\}$, the thermodynamic vector field F is zero. This means that every state in K is an equilibrium state.

Example 2: Heat flow. Consider compound system of two subsystems of ideal gas which exchange heat. We suppose that the volumes V_1, V_2 and quantities N_1, N_2 are fixed, so we have $K = \{(E_1,E_2)|E_1,E_2 > 0)\} = R_2^+$. Negentropy is $S = \sum_{i=1}^2 kN_i(\frac{5}{2}\ln N_i - \ln V_i - \frac{3}{2}\ln E_i + c)$, and we have a single process $\nu_1 = (1,-1)$. This means that energy is free to pass between the subsystems. For process form take $\lambda^{11} = DT_1T_2$, where $D > 0$ is a constant of thermal conductivity and $T_i = 2E_i/3kN_i = -(\partial S/\partial E_i)^{-1}$ are temperatures. Again, (K, S, ν, λ) is a closed system. We get

$$L = DT_1T_2 \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}, \quad \begin{array}{l} dE_1/dt = -DT_1T_2(\frac{\partial S}{\partial E_1} - \frac{\partial S}{\partial E_2}) = D(T_2 - T_1) \\ dE_2/dt = -DT_1T_2(\frac{\partial S}{\partial E_2} - \frac{\partial S}{\partial E_1}) = D(T_1 - T_2) \end{array}$$

The system has clearly the unique (equilibrium) stable stationary state, in which $T_1 = T_2$.

Since S is required to be extensive, it cannot be strictly convex. Because of the condition 5, $Im(\nu) \neq R_n$ and therefore $L(x)$ cannot be positive definite. However, it determines a positive definite form on $Im(\nu)$.

Proposition 1. For each $x \in K$ there exists a unique isomorphism $\ell(x) : Im(\nu)^* \to Im(\nu)$ such that $L(x) = \eta \circ \ell(x) \circ \eta^*$, where $\eta : Im(\nu) \to R_n$ is the inclusion.

Proof: There exists a unique surjective linear mapping $\rho : R_m \to Im(\nu)$ such that $\eta \circ \rho = \nu$. Define $\ell(x) = \rho \circ \lambda(x) \circ \rho^*$. Then ℓ has clearly the required properties.

$$
\begin{tikzcd}
R_n^* \arrow[rrr, dash, "L(x)"] \arrow[dd, dash, "\eta^*"'] \arrow[dr, phantom, "\nu^*"] & & & R_n \arrow[dd, dash, "\eta"] \arrow[dl, phantom, "\nu"'] \\
 & R_m^* \arrow[r, dash, "\lambda(x)"] & R_m & \\
Im(\nu)^* \arrow[rrr, dash, "\ell(x)"] \arrow[ur, phantom, "\rho^*"] & & & Im(\nu) \arrow[ul, phantom, "\rho"']
\end{tikzcd}
$$

Proposition 2. For each $x \in K$ the set $K_x = \{y \in K | y - x \in Im(\nu)\}$ is bounded and homeomorphic to an open subset of $Im(\nu)$. It is also an invariant set of the vector field F. We regard K_x as a manifold with tangent space $Im(\nu)$ at every point.

Proof: Suppose there exists a nonzero $y \in Im(\nu)$ such that for any $a > 0$ there is $x + ay \in K$. Since K is a cone, there is also $y + x/a \in K$ and therefore $y \in \overline{K}$, which is a contradiction with condition 5. Since K is open, K_x is open in $Im(\nu) + x$. Since $F(x) \in Im(\nu)$, F is a vector field on K_x, and therefore K_x is its invariant set.

The isomorphism $\ell(x)$ determines a bilinear form $\ell^\flat(x) : Im(\nu) \times Im(\nu) \to R$ by $\ell^\flat(x)(y, z) = ((\ell(x))^{-1}(y))(z)$. Since $L(x)$ is symmetric and positive semidefinite, $\ell(x)$ is symmetric and positive definite, so $\ell^\flat$ is a covariant (Riemannian) metric tensor on K_x. Furthermore $\ell^\#(x) : Im(\nu)^* \times Im(\nu)^* \to R$, defined by $\ell^\#(x)(u, v) = u(\ell(x)(v))$ is the corresponding contravariant metric tensor. Since $F(x) = -\ell(x)(dS(x))$ (here dS is the differential of S on $Im(\nu)$), F is the negative gradient of S with respect to this metric:

$$F = -grad_\ell S$$

Definition 3. The negentropy consumption $P : K \to R$ is

$$P(x) = -\frac{dS}{dt} = -dS(x)(F(x)) = \ell^\#(x)(dS(x), dS(x))$$

Clearly $P(x) \geq 0$ and if $P(x) = 0$, then $dS(x)(u) = 0$ for any $u \in Im(\nu)$. We prove now the existence of equilibrium.

Proposition 3. For each $x \in K$ there exists a unique state $\overline{x} \in K_x$, which we call equilibrium, where S attains its local as well as global minimum on K_x. For each $u \in Im(\nu)$ there is $dS(\overline{x})(u) = 0$ and the equilibrium is the only state with this property. Moreover each trajectory $x(t)$ of the thermodynamic vector field is defined for all $t > 0$, and $\lim_{t\to\infty} x(t) = \overline{x(0)}$.

Proof: For $\varepsilon > 0$ define $K_x^\varepsilon = \{y \in K_x | (\forall z \in \partial K)(|y - z| \geq \varepsilon)\}$. (Here $||$ is the Euclidean distance.) Because of condition 6, for each $z \in \partial K_x$ there exists $\varepsilon > 0$ such that in ε-neighbourhood of z, S is decreasing on the line connecting z to x. Since ∂K_x is compact, there exists the smallest such $\varepsilon > 0$, so for each $y \in K_x$ there is some $z \in K_x^\varepsilon$, such that $S(z) \leq S(y)$. Since ∂K_x^ε is compact, there exists a global minimum of S on K_x. Suppose that the global minimum were attained at two different states $y, z \in K_x$. Since d^2S is positive definite on $Im(\nu)$, S is strictly convex on K_x, and therefore $0 < a < 1$ implies $S(ay + (1-a)z) < aS(y) + (1-a)S(z) = S(y)$, which is a contradiction. So there is a unique $\overline{x} \in K_x$, where global minimum is attained. Suppose that $y \neq \overline{x}$ is a local minimum. Then $S(ay + (1-a)\overline{x}) < S(y)$ for all $0 < a < 1$, which is again a contradiction. Since $\overline{x}$ is a local minimum, $u \in Im(\nu)$ implies $dS(\overline{x})(u) = 0$. Conversely, if $y \neq \overline{x}$, then $dS(y, \overline{x} - y) < 0$, since S is strictly convex on $Im(\nu)$. To prove that equilibrium attracts all orbits, suppose that $(x(t))_{t\geq 0}$ is a trajectory of F. It follows from condition 6 that there is $\varepsilon > 0$ such that dS is bounded away from zero on $K_{x(0)} - K_{x(0)}^\varepsilon$, therefore there exists s such that $x(s) \in K_{x(0)}^\varepsilon$, and $K_{x(0)}^\varepsilon$ is invariant for F. It follows that $x(t)$ is defined for all $t > 0$. Suppose that $\overline{x(0)} \notin A = \overline{\{x(t)|t > 0\}}$ (here bar denotes the topological closure). Then $dS/dt < \varepsilon$ for some $\varepsilon > 0$ on A, and therefore $\lim_{t\to\infty} S(x(t)) = -\infty$, which is a contradiction. It follows that $\overline{x(0)} \in A$. Since $\overline{x(0)}$ is the only global minimum, for every its neighbourhood V there exists $\varepsilon > 0$, such that $\{y | S(y) < S(\overline{x(0)}) + \varepsilon\} \subseteq V$. It follows $\lim_{t\to\infty} x(t) = \overline{x(0)}$.

Definition 4. The negentropy surplus $R : K \to R_1$ is defined by

$$R(x) = S(x) - S(\overline{x})$$

Proposition 4.

$$R(x) = \sum_{i=1}^{n} x_i \left(\frac{\partial S(x)}{\partial x_i} - \frac{\partial S(\overline{x})}{\partial x_i} \right) \geq 0$$

Proof: Since S is extensive, we have $S(x) = \sum_{i=1}^{n} x_i (\partial S(x)/\partial x_i)$ by Euler theorem and therefore

$$R(x) = \sum_{i=1}^{n} x_i \left(\frac{\partial S(x)}{\partial x_i} - \frac{\partial S(\overline{x})}{\partial x_i} \right) + (x_i - \overline{x}_i) \frac{\partial S(\overline{x})}{\partial x_i}$$

Since $x - \overline{x} \in Im(\nu)$, the second term is zero.

3 Open thermodynamic systems

In open thermodynamic systems, the closed vector field F is superposed with a vector field G of the flows from environment. The flows may be constant or subject to condition that some intensive variables are kept constant. If $u \in R_n$ is a vector representing the flow, then $dS(x)(u)$ is an intensive function on K. Indeed for $a > 0$ we have $dS(ax)(u) = \lim_{t\to 0}(S(ax+tu) - S(ax))/t = dS(x)(u)$, since S is extensive. Thus the constraint of fixed temperature correponds to energy flow and the constraint of fixed concentration of some component correponds to the flow of this component.

Definition 5. An open thermodynamic system $(K, S, \lambda, \nu, \mu)$ consists of a closed thermodynamic system (K, S, λ, ν) and a linear mapping $\mu : K_p \to K_n$ of flows, such that d^2S is positive definite on $Im(\mu)$.

Proposition 5. Let $(K, S, \lambda, \nu, \mu)$ be an open thermodynamic system. Then there exists a unique vector field $G(x)$ on K such that

$$G(x) \in Im(\mu), \quad (\forall u \in Im(\mu))(d^2S(x)(u, F(x) + G(x)) = 0)$$

For $x \in K$ denote

$$K_x = \{y \in K | y - x \in Im(\nu) \oplus Im(\mu) \& (\forall u \in Im(\mu)(dS(x)(u) = dS(y)(u))\}$$

Then K_x is an invariant set of the vector field $F(x) + G(x)$.

Proof: The existence and uniqueness follows from the assumption that d^2S is positive definite on $Im(\mu)$ and therefore the mapping assigning to $u \in Im(\mu)$ the linear form $d^2S(u, -)$ is an isomorphism between $Im(\mu)$ and $Im(\mu)^*$. Clearly $F(x) + G(x) \in Im(\nu) \oplus Im(\mu)$ and if $u \in Im(\mu)$ then $dS(x)(u)$ is invariant for $F + G$ since $d^2S(x)(u, F(x) + G(x)) = 0$.

Definition 6. We call $F(x) + G(x)$ the (open) thermodynamic field of $(K, S, \lambda, \mu, \nu)$.

Example 3. Consider the closed thermodynamic system of Example 2 together with flow $\mu_1 = (0, 1)$. This means that energy is allowed to flow into the second subsystem from the environment. Since $\partial^2 S/\partial E_2^2 \neq 0$ the condition $d^2S(\mu_1, F + G) = 0$ gives $F^2 + G^2 = 0$. This yields thermodynamic vector field

$$\frac{dE_1}{dt} = D(T_2 - T_1), \; \frac{dE_2}{dt} = 0$$

so T_2 is kept konstant. The system has clearly the unique stable stationary state, in which $T_1 = T_2$.

Definition 7. The negentropy inflow $Q : K \to R_1$ is

$$Q(x) = dS(x)(G(x)) = \sum_{i=1}^{n} G^i(x) \frac{\partial S}{\partial x_i}$$

Proposition 6. For any trajectory $x(t)$ of an open thermodynamic system

$$\frac{dS(x)}{dt} = Q(x) - P(x) \ , \quad \frac{dR(x)}{dt} = Q(x) - P(x) - dS(\overline{x})(G(x))$$

Proof: The first formula follows immediately from the definition. To prove the second formula we have to show that $dS(\overline{x})/dt = dS(\overline{x})(G(x))$. Select a matrix $(\gamma_{ik})_{i=1,\ldots,n,k=1,\ldots,q}$ such that $Im(\nu) = Ker(\gamma)$ and the columns of γ are linearly independent. since $\sum_i \nu_j^i \gamma_{ik} = 0$, there is $\sum_i F^i(x)\gamma_{ik} = 0$. For a vector $x \in K$ denote $C_k = \sum_i x_i \gamma_{ik}$. The equilibrium vector $\overline{x}$ depends only on $C \in R_q$, and

$$\frac{dC_k}{dt} = \sum_i (F^i(x) + G^i(x))\gamma_{ik} = \sum_i G_i(x)\gamma_{ik} = \sum_i G_i(x) \frac{\partial C_k}{\partial x_i}$$

so

$$\frac{dS(\overline{x})}{dt} = \sum_k \frac{\partial S(\overline{x})}{\partial C_k} \frac{dC_k}{dt} = \sum_{k,i} \frac{\partial S(\overline{x})}{\partial C_k} \frac{\partial C_k}{\partial x_i} G_i(X) = dS(\overline{x})(G(x))$$

Example 4. Consider the open system from Example 3. Then

$$P = D(T_2 - T_1)^2/T_1T_2, \quad Q = D(T_1 - T_2)/T_2$$

$$R = \frac{3k}{2}(N_1 + N_2)(p_1 \ln \frac{p_1}{q_1} + p_2 \ln \frac{p_2}{q_2})$$

where $p_i = N_i/(N_1 + N_2)$, $q_i = E_i/(E_1 + E_2)$. In the stationary state P, Q and R vanish.

4 Chemical kinetics

Consider an ideal mixture of n chemical species $X_1, ..., X_n$ in a vessel of volume V, which react with each other under constant temperature. Denote N_i the number of molecules of the i-th species and $x_i = N_i/V$ its concentration. Since N_i and V are extensive variables, the state of the system is $(N_1, ..., N_n, V)$.

Let us suppose that the dynamics of the reactions is governed by the mass action law. It has been shown in [3] that this system has a Ljapunov function, which is the Helmholtz free energy function divided by gas constant, temperature and volume. This function plays the role of negentropy. A system of chemical reactions

$$\overset{+}{\nu}{}_j^1\ X_1 + ... + \overset{+}{\nu}{}_j^n\ X_n \ \underset{k_j^-}{\overset{k_j^+}{\rightleftharpoons}}\ \overset{-}{\nu}{}_j^1\ X_1 + ... + \overset{-}{\nu}{}_j^n\ X_n$$

is given by forward and backward reaction rates $k_j^+, k_j^- > 0$ and nonnegative stoichiometric vectors $\overset{+}{\nu}_j = (\overset{+}{\nu}{}_j^1, ..., \overset{+}{\nu}{}_j^n, 0)$, $\overset{-}{\nu}_j = (\overset{-}{\nu}{}_j^1, ..., \overset{-}{\nu}{}_j^n, 0)$ with integer entries.

Definition 8. We say that $\overset{+}{\nu}, \overset{-}{\nu}$: $R_m \to R_{n+1}$ are forwards and backwards stoichiometric matrices, if its entries are nonnegative integeres, their $(n+1)$-st columns are zero, and there exists a positive vector $m \in R_n^+$ such that $\sum_{i=1}^n (\overset{-}{\nu}{}_j^i - \overset{+}{\nu}{}_j^i) m_i = 0$. For $x \in R_n^+$ we denote

$$F_j^+(x) = k_j^+ \prod_{i=1}^n x_i^{\overset{+}{\nu}{}_j^i}, \quad F_j^-(x) = k_j^- \prod_{i=1}^n x_i^{\overset{-}{\nu}{}_j^i}$$

the forward and backwards reaction rates.

Proposition 8. Let $\overset{-}{\nu}, \overset{+}{\nu}$: $R_m \to R_{n+1}$ be stoichiometric matrices, $k^+, k^- \in R_m^+$ positive vectors of reaction rates, and $\alpha \in R_n^+$ a positive vector of entropic constants satisfying $F_j^+(\alpha) = F_j^-(\alpha)$ for any j. Denote

$$K = \{(N_1, ..., N_n, V) | N_i > 0, V > 0\}$$

$$S(N_1, ..., N_n, V) = \sum_{i=1}^n N_i (\ln N_i - \ln V - \ln \alpha_i - 1)$$

$$\nu = \overset{-}{\nu} - \overset{+}{\nu}$$

$$\lambda^{jj}(N_1, ..., N_n, V) = V \hbar(F_j^+(x), F_j^-(x)), \ \lambda^{jl} = 0 \ \text{ for } \ j \neq l$$

where $\hbar : R_2^+ \to R$ is defined on positive quadrant by

$$\hbar(x, y) = \frac{x - y}{\ln x - \ln y} \ \text{ for } x \neq y, \quad \text{and} \ \ \hbar(x, x) = x$$

Then (K, S, ν, λ) is a closed thermodynamic system, and its vector field is the mass action system

$$\frac{dx_i}{dt} = \sum_{j=1}^m (\overset{-}{\nu}{}_j^i - \overset{+}{\nu}{}_j^i)(F_j^+(x) - F_j^-(x))$$

Proof: Points 1,2,3,5 are straightforward. To prove 4, observe that $Im(\nu) \subseteq R_n = \{x \in R_{n+1} | x_n = 0\}$ and that d^2S is negative definite on R_n. Indeed $\partial^2 S/\partial N_i^2 = -1/N_i$, and $\partial^2 S/\partial N_i \partial N_j = 0$ for $i \neq j$. To prove 6, observe that $\lim_{N_i \to 0} \partial S/\partial N_i = \infty$. Since $\partial S/\partial N_i = \ln(x_i/\alpha_i)$, we have

$$\frac{dN_i}{dt} = -\sum_{jk} \nu_j^i \lambda^{jj}(x) \nu_j^k \ln \frac{x_k}{\alpha_k} = -\sum_{jk} \nu_j^i \lambda^{jj}(x) \left(\ln \frac{F_j^-(x)}{F_j^+(x)} - \ln \frac{F_j^-(\alpha)}{F_j^+(\alpha)} \right)$$

Since $F_j^+(\alpha) = F_j^-(\alpha)$,

$$\frac{dx_i}{dt} = \frac{1}{V} \sum_j \nu_j^i \lambda^{jj}(x) \ln \frac{F_j^+(x)}{F_j^-(x)} = \sum_j \nu_j^i (F_j^+(x) - F_j^-(x))$$

An open system is usually defined by constancy of some concentrations. For example if $u = (1, 0, ...0) \in Im(\mu)$, then $\partial S/\partial N_1 = \ln(x_1/\alpha_1)$ and therefore x_1 is kept constant. Because V is constant too, we characterize the system with specific negentropy $s = S/V$, specific negentropy consumption $p = P/V$, specific negentropy inflow $q = Q/V$, and specific negentropy surplus $r = R/V$. Then

$$s(x) = \sum_i x_i (\ln x_i - \ln \alpha_i - 1)$$

$$p(x) = \sum_j (F_j^+(x) - F_j^-(x))(\ln F_j^+(x) - \ln F_j^-(x))$$

$$q(x) = \sum_i G_i(x) \ln(x_i/\alpha_i)$$

$$r(x) = \sum_i x_i \ln(x_i/\overline{x_i}) + \sum_i (\overline{x_i} - x_i)$$

$$\frac{dr(x)}{dt} = -p(x) + \sum_{i=1}^n G_i(x) \ln(x_i/\overline{x_i})$$

Example 5: Autocatalysis. Consider a substrate X, intermediate product Y, and waste product Z with entropic constants

$$\alpha_X = k \ , \ \alpha_Y = 1 \ , \ \alpha_Z = 1/k \ , \ 0 < k < 1$$

Specific negentropy is $s(x, y, z) = x(\ln(x/k) - 1) + y(\ln y - 1) + z(\ln kz - 1)$. Consider reactions

$$X \underset{k}{\overset{1}{\rightleftharpoons}} Y \underset{k}{\overset{1}{\rightleftharpoons}} Z \ , \ X + 2Y \underset{ak}{\overset{a}{\rightleftharpoons}} 3Y \ , \ X + Y \underset{bk^2}{\overset{b}{\rightleftharpoons}} Y + Z$$

where $a, b > 0$. Thus $m_X = m_Y = m_Z = 1$ and $m = x + y + z$ is constant, so the equilibrium state for given m is $\overline{x} = mk^2/(1+k+k^2)$, $\overline{y} = mk/(1+k+k^2)$, $\overline{z} = m/(1+k+k^2)$. Stoichiometric matrices are

$$\overset{+}{\nu} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 2 & 0 \\ 1 & 1 & 0 \end{bmatrix}, \quad \overset{-}{\nu} = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 3 & 0 \\ 0 & 1 & 1 \end{bmatrix}, \quad \nu = \begin{bmatrix} -1 & , & 1 & , & 0 \\ 0 & , & -1 & , & 1 \\ -1 & , & 1 & , & 0 \\ -1 & , & 0 & , & 1 \end{bmatrix}$$

$$\lambda^{11} = \hbar(x, ky),\ \lambda^{22} = \hbar(y, kz),\ \lambda^{33} = \hbar(axy^2, aky^3),\ \lambda^{44} = \hbar(bxy, bk^2yz)$$

$$L^{ik}(x,y,z) = \begin{bmatrix} \lambda^{11} + \lambda^{33} + \lambda^{44} & , & -\lambda^{11} - \lambda^{33} & , & -\lambda^{44} \\ -\lambda^{11} - \lambda^{33} & , & \lambda^{11} + \lambda^{22} + \lambda^{33} & , & -\lambda^{22} \\ -\lambda^{44} & , & -\lambda^{22} & , & \lambda^{22} + \lambda^{44} \end{bmatrix}$$

If we introduce coordinates (u, v) on $K_{(\overline{x},\overline{y},\overline{z})}$ via

$$(x, y, y) = (\overline{x}, \overline{y}, \overline{z}) + u(-1, 1, 0) + v(0, -1, 1)$$

then $\rho : R_m \to Im(\nu)$, $\eta : Im(\nu) \to R_n$, and the covariant metric tensor ℓ^{ik} are

$$\rho = \begin{bmatrix} 1 & 0 \\ 0 & 1 \\ 1 & 0 \\ 1 & 1 \end{bmatrix}, \quad \eta = \begin{bmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \end{bmatrix}, \quad \ell^{ik} = \begin{bmatrix} \lambda^{11} + \lambda^{33} + \lambda^{44} & , & \lambda^{44} \\ \lambda^{44} & , & \lambda^{22} + \lambda^{44} \end{bmatrix}$$

The closed thermodynamic vector field is

$$\begin{aligned} dx/dt &= -(1 + ax^2)(x - ky) - by(x - k^2z) \\ dy/dt &= (1 + ax^2)(x - ky) - (y - kz) \\ dz/dt &= (y - kz) + by(x - k^2z) \end{aligned}$$

An open system may be defined by keeping the concentrations of substrate X and product Z constant. This corresponds to matrix

$$\mu = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

We get $dx/dt = dy/dt = 0$, so

$$\begin{aligned} G_x(x,y,z) &= (1 + ax^2)(x - ky) + by(x - k^2z) \\ G_y(x,y,z) &= 0 \\ G_z(x,y,z) &= -(y - kz) - by(x - k^2z) \end{aligned}$$

and the negentropy inflow may be evaluated.

References

[1] Akin,E.: The Geometry of Population Genetics. Lecture Notes in Biomathematics 31. Springer-Verlag, Berlin, 1979.

[2] Callen,H.B.: Thermodynamics. John Wiley & Sons, New York, 1960.

[3] Horn,F.,Jackson,R: General mass action kinetics. Arch. Ration. Mech. Anal. 47 (1972) 81.

[4] Nicolis,G., Prigogine,I.: Self-Organization in Nonequilibrium Systems. From Dissipative Systems to Order through Fluctuations. J.Wiley & Sons, New York, 1977.

[5] Roberts,A.W., Varberg,D.E.: Convex Functions. Academic Press, New York, 1973.

[6] Rockafellar,R.Tyrell: Convex Analysis. Princeton University Press, Princeton, 1970.

[7] Schrödinger,E.: What is Life? Cambridge University Press, London, 1944.

[8] Šilhavý,M.: On measures, convex cones, and foundations of thermodynamics, I & II. Czech. J. Phys. B 30 (1980), 841; 961.

[9] Straumann,N.: Thermodynamik. Springer-Verlag, Berlin, 1986.

[10] Truesdell,C.: Rational Thermodynamics. Springer-Verlag, Berlin, 1984.