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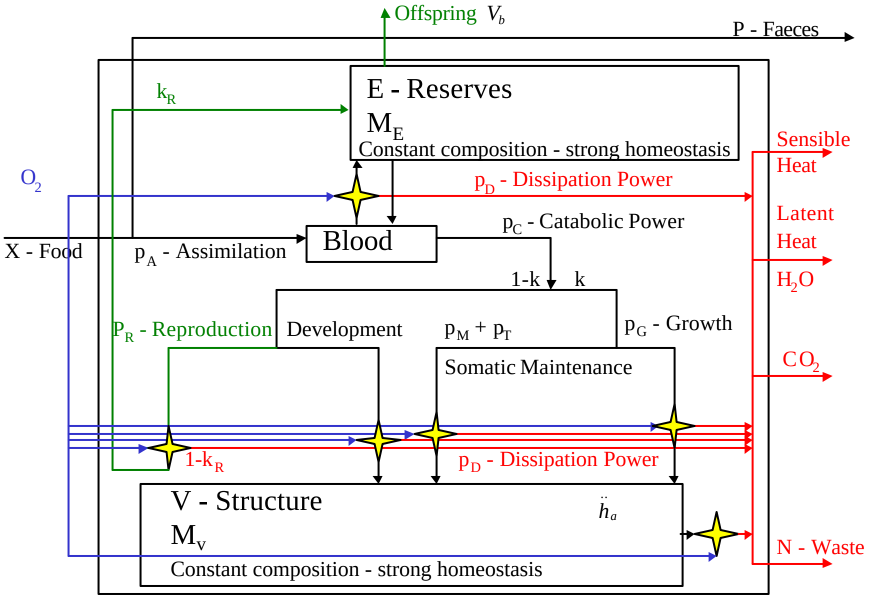
Essay of the Dynamic Energy Budget Course

Thermodynamic Formalism of Biological Systems in the DEB Theory

In this essay we intend to discuss the possibilities of integration of the second law of thermodynamics in the DEB theory by performing an entropy balance of an individual described as in the DEB theory. First we present the mass and energy balances in a slightly different way. Kooijman B. (2000) presents equations regarding the mass balance (equation 4.2) and the energy balance (equation 4.36). These equations do not conform with the usual distinction between fluxes in and out the frontier and changes internal to the system under study. We think it is important to present them following the traditional thermodynamic analysis so the entropy balance and its interpretation follow more easily. Next we discuss the entropy balance and present future developments of this essay.

We start by defining our thermodynamic system, an organism (excluding plants), sumarising and schematizing the dynamic energy and mass budgets in biological theory developed by Bas Kooijman (2000). The thick line is the organism's outter surface, its frontier. Food enters, X, and splits between faeces, P, that exit the organism and assimilated food. The energy of the food assimilated is termed the assimilation power, p_A. The blood provides the reserve, E, with a mass flux (assimilated food) that is converted through a chemical reaction (star points) into the reserve chemical composition. This reaction, like all other reactions receive oxygen (in blue) and have as final nonwanted products heat, CO_2 and nitrogeneous waste. The sum of the nonwanted products is called the dissipation power, p_D (in red). The reserve chemical composition is constant due to the strong homeostasis assumption. The reserve 'feeds' the blood. The energy in the blood that is consumed by the structural tissues is called the catabolic power, p_c. This energy flux is partioned accordingly to the k-rule that allocates a fixed k fraction of this flux to growth, p_G, plus somatic maintenance, p_M+p_T, and the remain fraction to development plus reproduction, p_R. The synthesis of new structure mass occurs through chemical reactions where a fraction of the growth energy flux ends up as dissipation power. According to Kooijman B. (2000) maintenance processes include 'the maintenance of concentration gradients across membranes, the turnover of structural body proteins…and movement'. Development is the energy flux that permits an increasing complexity of the structure volume.

ORGANISM - DEB THEORY



We now apply the standard mass, energy and entropy balances for open systems (Moran et al., 2000),

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out}$$

$$\frac{dE}{dt} = \dot{Q} + \dot{W} + \dot{m}_{in}\left(h_{in} + \frac{v_{in}^{2}}{2} + gz_{in} \right) - \dot{m}_{out}\left(h_{out} + \frac{v_{out}^{2}}{2} + gz_{out} \right),$$

$$\frac{dS}{dt} = \dot{s} + \frac{\dot{Q}}{T} + s_{in}\dot{m}_{in} - s_{out}\,\dot{m}_{out}$$

to the thermodynamic system described above.

Mass Balance Equation

The mass balance equation presented tells us that the rate of change of mass contained within the control volume of our thermodynamic system equals the inputs minus the outputs. Our system is composed by one reserve and structural volume, the mass contained in the blood is neglected according to Kooijman B. (2000). The food is an organic input and the faeces is an organic output. The mineral inputs and outputs comprise O_2, nitrogenous waste, CO_2 and the formation of water inside the organism.

$$\begin{bmatrix} n_{CV} & n_{CE} \\ n_{HV} & n_{HE} \\ n_{OV} & n_{OE} \\ n_{NV} & n_{NE} \end{bmatrix} \begin{bmatrix} dM_V/dt \\ d\left(M_E + M_{ER}\right)/dt \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & n_{CN} \\ 0 & 2 & 0 & n_{HN} \\ 2 & 1 & 2 & n_{ON} \\ 0 & 0 & 0 & n_{NN} \end{bmatrix} \begin{bmatrix} \dot{J}_C \\ \dot{J}_H \\ \dot{J}_O \\ \dot{J}_N \end{bmatrix} + \begin{bmatrix} n_{CX} & n_{CP} \\ n_{HX} & n_{HP} \\ n_{OX} & n_{OP} \\ n_{NX} & n_{NP} \end{bmatrix} \begin{bmatrix} \dot{J}_X \\ \dot{J}_P \end{bmatrix}$$

The strong homeosis hypothesis states that the chemical composition of both the structural volume and the reserves do not change and therefore the first matrix is constant. The fluxes $\dot{J}_i$ are positive if they represent a net input and negative otherwise. This equation is simply a manipulation of the DEB mass balance equation in which we identify the accumulation of mass term with the rate of change of reserve and structural mass.

Energy Balance Equation

Energy Balance Equation to our Thermodynamic System

According to Garby et al (1995, pp 109) ‘the product pv is generally very small in comparison with the enthalpy of formation for compounds in biological systems’ and therefore $u = h - pv \Rightarrow u \cong h$. With this simplification the energy balance of the entire thermodynamic system is:

$$\begin{bmatrix} n_{CV}(m_C + Ts_C) & n_{CE}(m_C + Ts_C) \\ n_{HV}(m_H + Ts_H) & n_{HE}(m_H + Ts_H) \\ n_{OV}(m_O + Ts_O) & n_{OE}(m_O + Ts_O) \\ n_{NV}(m_N + Ts_N) & n_{NE}(m_N + Ts_N) \end{bmatrix} \begin{bmatrix} dM_V/dt \\ d(M_E + M_{ER})/dt \end{bmatrix} =$$

$$\begin{bmatrix} (m_C + Ts_C) & 0 & 0 & (m_C + Ts_C)n_{CN} \\ 0 & 2(m_H + Ts_H) & 0 & (m_H + Ts_H)n_{HN} \\ 2(m_O + Ts_O) & (m_O + Ts_O) & 2(m_O + Ts_O) & (m_O + Ts_O)n_{ON} \\ 0 & 0 & 0 & (m_N + Ts_N)n_{NN} \end{bmatrix} \begin{bmatrix} \dot{J}_C \\ \dot{J}_H \\ \dot{J}_O \\ \dot{J}_N \end{bmatrix} + \begin{bmatrix} (m_C + Ts_C)n_{CX} & (m_C + Ts_C)n_{CP} \\ (m_H + Ts_H)n_{HX} & (m_H + Ts_H)n_{HP} \\ (m_O + Ts_O)n_{OX} & (m_O + Ts_O)n_{OP} \\ (m_N + Ts_N)n_{NX} & (m_N + Ts_N)n_{NP} \end{bmatrix} \begin{bmatrix} \dot{J}_X \\ \dot{J}_P \end{bmatrix} + \dot{Q}_{conv+rad+latent}$$

where the work is null because the work of the control volume is given by -∫vdP (Moran, 2000, pp290) and the enthalpy was substituted by:

$$H_i = U_i + PV_i = G_i + TS_i = N_i(m_i + Ts_i)$$

The heat in this energy balance is the heat exchanged by the organism and its surroundings. This heat transfer is divided in convection, conduction and radiation. It is important to mention that in convection it is used the temperature of the body surface and that of the environment, whereas in radiation it is used the temperature of the sky, defined as a function of the temperature of the surroundings. In general the temperature of the sky and the environment are not the same.

Energy Balance Equation to the Reactions Points

We think equation 4.36 (Kooijman, 2000) is an energy balance to the ‘points’ where the reactions take place (star points presented on the scheme above). This abstraction makes sense considering that the reactions occur at reactors with negligible mass. The heat that appears in equation 4.36 is the total heat released in all those reactions whereas, the heat in the balance equation we derived must be the sensible and latent heat exchanged with the surroundings.

If the energy balance equation is applied to one of these ‘reaction points’ we obtain,

$$\underbrace{\frac{dE}{dt}}_{\substack{=0\text{(thermodynamic} \\ \text{system has negligible mass)}}} = \dot{Q} - \underbrace{\dot{W}}_{=0\text{(work is null)}} + \dot{m}_{in}h_{in} - \dot{m}_{out}h_{out} \Leftrightarrow$$

$$0 = \dot{Q} + \dot{m}_{in}g_{in} - \dot{m}_{out}g_{out} = \dot{Q} + \dot{m}_{in}m_{in} - \dot{m}_{out}m_{out}$$

since the work is null and the accumulation of energy is also null due to the fact that the reactors have negligible mass. The equality between the enthalpy and the Gibbs free energy is made using the empirical knowledge stated in Garby et al (1995, pp 152) where 'for some of the most important reactions in biological systems' the term $T\Delta s$ is very small compared to Δh, leading to the following,

$$g = h - Ts \Rightarrow dg = dh - Tds - \underbrace{sdT}_{=0 \text{ (T is constant)}} \cong dh\,.$$

If we apply the balance energy equation to all reaction points together we get,

$$0 = Q + m\dot{N}$$

$$0 = Q_{reactions} + \begin{bmatrix} m_C n_{CX} & m_C n_{CP} \\ m_H n_{HX} & m_H n_{HP} \\ m_O n_{OX} & m_O n_{OP} \\ m_N n_{NX} & m_N n_{NP} \end{bmatrix} \begin{bmatrix} \dot{J}_X \\ \dot{J}_P \end{bmatrix} + \begin{bmatrix} m_C & 0 & 0 & m_C n_{CN} \\ 0 & 2m_H & 0 & m_H n_{HN} \\ 2m_O & m_O & 2m_O & m_O n_{ON} \\ 0 & 0 & 0 & m_N n_{NN} \end{bmatrix} \begin{bmatrix} \dot{J}_C \\ \dot{J}_H \\ \dot{J}_O \\ \dot{J}_N \end{bmatrix} - \begin{bmatrix} m_C n_{CV} & m_C n_{CE} \\ m_H n_{HV} & m_H n_{HE} \\ m_O n_{OV} & m_O n_{OE} \\ m_N n_{NV} & m_N n_{NE} \end{bmatrix} \begin{bmatrix} dM_V/dt \\ d(M_E + M_{ER})/dt \end{bmatrix}$$

which is equivalent to equation 4.36 (Kooijman, 2000) because the total reaction heat must be equal to the total thermal fluxes between the organism and the environment. This results from an energy balance to the outer surface of the organism.

Replacing the heat, Q, in the total energy balance by the last equation the following is obtained,

$$\begin{bmatrix} n_{CV}(Ts_C) & n_{CE}(Ts_C) \\ n_{HV}(Ts_H) & n_{HE}(Ts_H) \\ n_{OV}(Ts_O) & n_{OE}(Ts_O) \\ n_{NV}(Ts_N) & n_{NE}(Ts_N) \end{bmatrix} \begin{bmatrix} dM_V/dt \\ d(M_E + M_{ER})/dt \end{bmatrix} =$$

$$\begin{bmatrix} (Ts_C) & 0 & 0 & (Ts_C)n_{CN} \\ 0 & 2(Ts_H) & 0 & (Ts_H)n_{HN} \\ 2(Ts_O) & (Ts_O) & 2(Ts_O) & (Ts_O)n_{ON} \\ 0 & 0 & 0 & (Ts_N)n_{NN} \end{bmatrix} \begin{bmatrix} \dot{J}_C \\ \dot{J}_H \\ \dot{J}_O \\ \dot{J}_N \end{bmatrix} + \begin{bmatrix} (Ts_C)n_{CX} & (Ts_C)n_{CP} \\ (Ts_H)n_{HX} & (Ts_H)n_{HP} \\ (Ts_O)n_{OX} & (Ts_O)n_{OP} \\ (Ts_N)n_{NX} & (Ts_N)n_{NP} \end{bmatrix} \begin{bmatrix} \dot{J}_X \\ \dot{J}_P \end{bmatrix}\,.$$

Entropy Balance Equation

The motivation for calculating the entropy balance equation is related to the fact that throughout the DEB theory, the author argues that entropy and the irreversibilities of the processes are much too complicated to be calculated. As long as the minerals fluxes are specified their entropy can be calculated. Also, since the organic fluxes are specified their entropy can also be calculated. At this point is relevant to mention that for the specification of the organic compounds in the organism some simplifications are necessary, such as the homeostasis assumptions. Nevertheless, DEB theory provides good arguments to the definition of a generalized biomass composition that is present and constant in a large number of organisms.

About the specification of the processes inside the organism, we argue that these can be known by using information on the net mass fluxes of the organism, as discussed below.

The entropy balance to the organism is,

$$\begin{bmatrix} s_C n_{CV} & s_C n_{CE} \\ s_H n_{HV} & s_H n_{HE} \\ s_O n_{OV} & s_O n_{OE} \\ s_N n_{NV} & s_N n_{NE} \end{bmatrix} \begin{bmatrix} dM_V/dt \\ d(M_E + M_{ER})/dt \end{bmatrix} = \dot{s} + \frac{Q_{reactions}}{T} + \begin{bmatrix} s_C n_{CX} & s_C n_{CP} \\ s_H n_{HX} & s_H n_{HP} \\ s_O n_{OX} & s_O n_{OP} \\ s_N n_{NX} & s_N n_{NP} \end{bmatrix} \begin{bmatrix} \dot{J}_X \\ \dot{J}_P \end{bmatrix} + \begin{bmatrix} s_C & 0 & 0 & s_C n_{CN} \\ 0 & 2s_H & 0 & s_H n_{HN} \\ 2s_O & s_O & 2s_O & s_O n_{ON} \\ 0 & 0 & 0 & s_N n_{NN} \end{bmatrix} \begin{bmatrix} \dot{J}_C \\ \dot{J}_H \\ \dot{J}_O \\ \dot{J}_N \end{bmatrix} .$$

It is convenient to find an expression for the irreversibility term, $T\dot{s}$. This term is related to the irreversibilities (Garby et al, 1995) created in internal processes. The specification of the entire machinery of the organism can be avoided, using the energy balance equations to the organism and to the reaction points. So, the last equation can be simplified if the heat is replaced,

$$\frac{1}{T} \begin{bmatrix} (Ts_C - m_C)n_{CV} & (Ts_C - m_C)n_{CE} \\ (Ts_H - m_H)n_{HV} & (Ts_H - m_H)n_{HE} \\ (Ts_O - m_O)n_{OV} & (Ts_O - m_O)n_{OE} \\ (Ts_N - m_N)n_{NV} & (Ts_N - m_N)n_{NE} \end{bmatrix} \begin{bmatrix} dM_V/dt \\ d(M_E + M_{ER})/dt \end{bmatrix} = \dot{s} + \frac{1}{T} \begin{bmatrix} (Ts_C - m_C)n_{CX} & (Ts_C - m_C)n_{CP} \\ (Ts_H - m_H)n_{HX} & (Ts_H - m_H)n_{HP} \\ (Ts_O - m_O)n_{OX} & (Ts_O - m_O)n_{OP} \\ (Ts_N - m_N)n_{NX} & (Ts_N - m_N)n_{NP} \end{bmatrix} \begin{bmatrix} \dot{J}_X \\ \dot{J}_P \end{bmatrix} +$$

$$\frac{1}{T} \begin{bmatrix} (Ts_C - m_C) & 0 & 0 & (Ts_C - m_C)n_{CN} \\ 0 & 2(Ts_H - m_H) & 0 & (Ts_H - m_H)n_{HN} \\ 2(Ts_O - m_O) & (Ts_O - m_O) & 2(Ts_O - m_O) & (Ts_O - m_O)n_{ON} \\ 0 & 0 & 0 & (Ts_N - m_N)n_{NN} \end{bmatrix} \begin{bmatrix} \dot{J}_C \\ \dot{J}_H \\ \dot{J}_O \\ \dot{J}_N \end{bmatrix}$$

Further, using the last form of the energy balance for the entire organism we get,

$$-\frac{1}{T} \begin{bmatrix} m_C n_{CV} & m_C n_{CE} \\ m_H n_{HV} & m_H n_{HE} \\ m_O n_{OV} & m_O n_{OE} \\ m_N n_{NV} & m_N n_{NE} \end{bmatrix} \begin{bmatrix} dM_V/dt \\ d(M_E + M_{ER})/dt \end{bmatrix} = \dot{s} - \frac{1}{T} \begin{bmatrix} m_C n_{CX} & m_C n_{CP} \\ m_H n_{HX} & m_H n_{HP} \\ m_O n_{OX} & m_O n_{OP} \\ m_N n_{NX} & m_N n_{NP} \end{bmatrix} \begin{bmatrix} \dot{J}_X \\ \dot{J}_P \end{bmatrix}$$

$$-\frac{1}{T} \begin{bmatrix} m_C & 0 & 0 & m_C n_{CN} \\ 0 & 2m_H & 0 & m_H n_{HN} \\ 2m_O & m_O & 2m_O & m_O n_{ON} \\ 0 & 0 & 0 & m_N n_{NN} \end{bmatrix} \begin{bmatrix} \dot{J}_C \\ \dot{J}_H \\ \dot{J}_O \\ \dot{J}_N \end{bmatrix} .$$

$$T\dot{s}=+\begin{bmatrix} m_C n_{CX} & m_C n_{CP} \\ m_H n_{HX} & m_H n_{HP} \\ m_O n_{OX} & m_O n_{OP} \\ m_N n_{NX} & m_N n_{NP} \end{bmatrix}\begin{bmatrix} \dot{J}_X \\ \dot{J}_P \end{bmatrix}+\begin{bmatrix} m_C & 0 & 0 & m_C n_{CN} \\ 0 & 2m_H & 0 & m_H n_{HN} \\ 2m_O & m_O & 2m_O & m_O n_{ON} \\ 0 & 0 & 0 & m_N n_{NN} \end{bmatrix}\begin{bmatrix} \dot{J}_C \\ \dot{J}_H \\ \dot{J}_O \\ \dot{J}_N \end{bmatrix}$$

$$-\begin{bmatrix} m_C n_{CV} & m_C n_{CE} \\ m_H n_{HV} & m_H n_{HE} \\ m_O n_{OV} & m_O n_{OE} \\ m_N n_{NV} & m_N n_{NE} \end{bmatrix}\begin{bmatrix} dM_V/dt \\ d\left(M_E+M_{ER}\right)/dt \end{bmatrix}=Q_{reactions}$$

which shows that the irreversibilities created inside the organism can be specified by the net fluxes of chemical compounds in and out of the organism. It is also noted that the irreversibility is equal to the heat released in the reactions inside the organism. Therefore, since the second law tells us that the entropy production is positive, the total heat released by the chemical reactions is also positive. This result is weaker than the result presented by Koiijman (2000): ‘the second law of thermodynamics implies that the processes of assimilation, dissipation and growth are exothermic’.

Matter vs Energy

Koiijman B. (2000) considers that matter can be converted to energy through a coefficient μ_{*1*2} that ‘couples energy flux $_{*1}$ to mass flux $_{*2}$’. We agree with Koiijman B.(2000) that the energy of a mass flux is given by its enthalpy but we don’t think as the author does that ‘for many practical purposes…enthalpies can be substituted for free energies.’ In fact, the assumption that term $T\boldsymbol{D}s$ is very small compared to $\boldsymbol{D}h$ allowed us to derive the energy and entropy balances and is a less problematic assumption. Garby et al. (1995) has examples of calculated entalpies and entropies for common organic and mineral compounds for biological systems which hint that enthalpies should not be substituted for free energies. We believe that enthalpies need not to be substituted for free energies.

Future Developments

The DEB theory assumes that there is a certain rate of formation of damaged DNA that we believe might be useful to relate to the entropy in the organism. We believe that the entropy of the organism increases with the damaged DNA and decreases with maturity/complexity. Therefore we think that could be useful to separate the structural mass into ‘damaged’ structural mass characterised by a higher specific entropy, s_Q, and ‘normal’ structural mass characterised by a lower specific entropy, s_V. The increase in maturity/complexity would be translated into a s_V that decreases with development state. The increase of damaged to normal structural mass would be a function of the total oxygen flux, as suggested by Koiijman B. (2000).

The relation between μ_* and μ_{*1*2} seemed us quit interesting since it is most used in the DEB theroy for deriving relevant results. We believe this assumption needs more argumentation.

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