

Research Paper

Entropy-Production and Exergy in the Thermodynamic Modelling of Ecosystem

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Abstract: *The object of the paper is to study the relation between the concepts of entropy and exergy in the non-equilibrium thermodynamic modelling of ecosystems. We have first found out the expression of exergy of a multi component ecosystem on the basis of the ideal gas model of the ecosystem and studied its relation with the expression of entropy-production in the development of the thermodynamics of ecosystem. We have next developed a statistical model of the ecosystem and determined the law of probability distribution of the macro-state of the ecosystem involving the expression of exergy of the ecosystem. On the basis of the probability distribution of macro-states, we have investigated the criteria of stability and instability consistent with Jorgensen's principle of increasing of exergy with evolution.*

Keywords: Ecosystem, Thermodynamic Model, Entropy and Exergy, Criteria of Stability and Evolution, Exergy Principle.

Introduction

An ecosystem consisting of a multiple of components or species is an open thermodynamic system exchanging energy, nutrient, biomass with the environment. Ecosystem development shows irreversible and non-repeatable history, a tendency expressed by the second law of thermodynamics. Besides the balance equation of mass and energy of all components of the ecosystem, the second law of thermodynamics must inevitably be taken into account. All processes within the ecosystem are of irreversible type, all producing entropy. The entropy-production plays a vital role in the thermodynamic theory of ecosystem. In recent years, great efforts are going on in explaining the structure and function of ecosystems in the light of non-equilibrium thermodynamic models of ecosystems [1-6]. In some

recent papers we have developed non-equilibrium thermodynamic models of ecosystems and made entropic analysis of irreversibility associated with the structure, organization, stability, diversity, complexity and evolution of complex ecosystem [7-9].

In the present paper we have introduced another thermodynamic quantity of significant importance in the modelling of complex ecosystems. This is the concept of exergy introduced first in ecological modelling by Majer and Jorgensen [2]. We have first developed a thermodynamic model of ecosystem and found out the expression of exergy on the basis of the ideal gas model of the ecosystem. We have investigated its (exergy) relation with the expression of entropy-production of the ecosystem. We have next developed a statistical mechanical model of the multicomponent ecosystem. This is possible in view of the many body aspect of the ecosystem. The statistical model based on generalized Boltzmann-Shannon entropy leads to the probability distribution of the macrostate involving the expression of exergy of the ecosystem. The derivation is consistent with the negentropy concept of exergy [2,3]. The statistical model provides the probabilistic support to the deterministic criteria of stability and instability involving evolution of the ecosystem consistent with Jorgensen's principle of increasing exergy for evolution.

Thermodynamic Model: Entropy-Production and Exergy-Function

Let us consider a multi-component ecosystem, say A , immersed in an environment A_0 (say). Let $N = (N_1, N_2, \dots, N_n)$ be the population sizes (or densities) of the different components or species of the ecosystem at any time t . In the thermodynamic model of the system it represents the macro-state of the ecosystem. Let $N^* = (N_1^*, N_2^*, \dots, N_n^*)$ represents the stationary or thermodynamic equilibrium state of the system with the environment. Let T and T_0 be the temperatures, p and p_0 be the pressures, μ_i and μ_i^0 be the chemical potentials of the i th component or species for the non-stationary (or non-equilibrium) and the stationary (or thermodynamic equilibrium) states respectively. When we want to describe the behaviour and properties of the open system which is connected very closely with the surrounding environment (this is a typical definition of an ecosystem), the concept of work done by the system on its environment and the work done by the environment on the system enclosed within it play a significant role. Infact, exergy E_x is defined as the amount of work that a system can perform when it is brought into the thermodynamic equilibrium with its environment and according to Jorgensen it is defined in the differential form as [2]

$$dE_x = (T - T_0)dS - (p - p_0)dV + \sum_{i=1}^n (\mu_i - \mu_i^0)dN_i \quad (2.1)$$

where S is the entropy and V is the volume of the ecosystem. At the thermodynamic equilibrium between the system A and its environment A_0 , $T = T_0$, $p = p_0$, $\mu_i = \mu_i^0$ for every i . We have then

$$dE_x = 0 \quad (2.2)$$

implying the extreme value of the exergy at thermodynamic equilibrium. We now consider the non-equilibrium state when pressure and temperature of the ecosystem coincide with those of the environment, that is, $p = p_0$, $T = T_0$. The expression of exergy (2.1) then reduces to the form

$$dE_x = \sum_{i=1}^n (\mu_i - \mu_i^0)dN_i \quad (2.3)$$

which is the expression of the difference of entropy free energies. We now consider ideal gas model of

the ecosystem [10]. Then for the i th species or component, we have the chemical potential μ_i as [10]

$$\mu_i = \mu_i^0 + RT \ln \frac{N_i}{N_i^*} \quad (2.4)$$

where R is the gas constant and is given by $R = kN_a$, where k is the Boltzmann constant and N_a is the Avogadro's number. The expression (2.3) then reduces to the form

$$dE_x = RT \sum_{i=1}^n \ln \frac{N_i}{N_i^*} dN_i \quad (2.5)$$

Integrating (2.5) from the thermodynamic equilibrium state N^* to the non-equilibrium state N , we have

$$E_x(N^* \rightarrow N) = RT \sum_{i=1}^n [N_i \ln \frac{N_i}{N_i^*} - (N_i - N_i^*)] \quad (2.6)$$

which is the expression of exergy function for transition ($N^* \rightarrow N$) of the system.

Let us now investigate the relationship between the concept of exergy with the concept of entropy-production or dissipation of energy in non-equilibrium thermodynamics. In the case of open system the change of the entropy is the sum of two terms:

$$dS(t) = d_i S(t) + d_e S(t) \quad (2.7)$$

where $d_e S$ is the result of exchange between the system and environment and $d_i S$ is the entropy-produced within the system as a result of internal spontaneous irreversible processes within the system. In thermodynamics of irreversible processes the rate of entropy-production is given by [11, 12]

$$\frac{d_i S(t)}{dt} = \frac{1}{T} \sum_{i=1}^n X_i J_i \quad (2.8)$$

where X_i and J_i are the thermodynamic forces and fluxes respectively. For the ideal gas model of the system under consideration the thermodynamic forces are given by the affinity for the transition ($N_i \rightarrow N_i^*$)

$$X_i = \mu_i - \mu_i^* = RT \ln \frac{N_i}{N_i^*} \quad (i = 1, 2, \dots, n) \quad (2.9)$$

and the corresponding thermodynamic fluxes J_i are given by

$$J_i = \frac{dN_i}{dt} \quad (i = 1, 2, \dots, n) \quad (2.10)$$

Then the entropy-produced in transition from the non-equilibrium state N to the thermodynamic equilibrium state N^* is given by

$$S(N \rightarrow N^*) = S^0 - S = \Delta_i S = \frac{1}{T} \int_N^{N^*} X_i J_i dt$$

$$= \frac{1}{T} \int_N^{N^*} \frac{dN_i}{dt} RT \ln \frac{N_i}{N_i^*} dt = -R \sum_{i=1}^n [N_i \ln \frac{N_i}{N_i^*} - (N_i - N_i^*)] \quad (2.11)$$

We see that $\Delta S < 0$ for any $N_i > 0$ (except for $N_i = N_i^*$ when $\Delta S = 0$). It implies that for any open system for the transition of the system from non-stationary (or non-equilibrium) state to stationary or thermodynamic equilibrium state, the total change of entropy is negative. The expression of dissipative function i.e., the energy dissipated for the transition ($N \rightarrow N^*$) is given by

$$\begin{aligned} Diss(N \rightarrow N^*) &= \int_N^{N^*} RT \ln \frac{N_i}{N_i^*} dN_i \\ &= RT \int_N^{N^*} \ln \frac{N_i}{N_i^*} \frac{dN_i}{dt} dt = TS(N \rightarrow N^*) \end{aligned} \quad (2.12)$$

so that we have the relation between the dissipation function and entropy-production as

$$Diss(N \rightarrow N^*) = TS(N \rightarrow N^*) = T\Delta_i S \quad (2.13)$$

From (2.6), (2.11) and (2.13) we have the relation between the exergy-function, dissipation function and entropy-production as

$$E_x(N^* \rightarrow N) = -Diss(N \rightarrow N^*) = -T\Delta_i S \quad (2.14)$$

which shows that the transition of the system from the thermodynamic equilibrium state N^* to the non-equilibrium state N is accompanied with a dissipation of energy. The negativeness of the dissipation $Diss(N \rightarrow N^*)$ (or equivalently the entropy-production $\Delta_i S$) implies that the transition from some thermodynamic equilibrium state to non-equilibrium state is not spontaneous, but forced [2]. For spontaneous processes (when the system is closed and it moves to an equilibrium state after a small internal fluctuation) the transition from non stationary (non-equilibrium) state to the stationary or equilibrium state ($N \rightarrow N^*$) is accompanied by the increase of entropy. In the case of open ecosystem the transition ($N \rightarrow N^*$) is not spontaneous but forced, it depends on the interaction between the system and its environment. The decrease of entropy or dissipation is a result of free-energy consumption by the system from the environment. It is the result of exchange processes with the environment which gives a negative contribution into the entropy-production or dissipation-function. According to the definition of exergy (2.6) it is equal to the absolute value of the entropy decrease [2].

Statistical Model: Exergy-Function and Exergy Principle

Let us now consider the statistical model of the open multi-component system consisting of n components or species. The macroscopic state of the system at time t is given by the set of populations $N = (N_1, N_2, \dots, N_n)$. In view of the many-body aspect of the system, the numbers (N_1, N_2, \dots, N_n) are assumed to be random variables and the system is amenable to the methods of statistical mechanics. The main problem of statistical model is to find out the probability distribution of $N_i, (i = 1, 2, \dots, n)$. Let $p(N_i)$ be the probability distribution of $N_i, (i = 1, 2, \dots, n)$. The entropy of the i th component or species is assumed to be governed by the generalized Boltzmann-Gibbs entropy [13-14].

$$S(P|W) = \sum_{\{N_i\}} p(N_i) \ln \frac{p(N_i)}{W(N_i)} \tag{3.1}$$

where the summation is over all possible values of N_i , $W(N_i)$ is some measurable function of N_i defined over the N_i -space and constitutes the prior information about N_i . This measure according to classical statistical mechanics is given by [13, 14]

$$W(N_i) = \frac{1}{N_i!} \tag{3.2}$$

The main problem of the statistical model is to estimate the probability distribution $p(N_i)$ on the basis of some available information. Let the available information constitutes the average values:

$$\sum_{\{N_i\}} N_i p(N_i) = \bar{N}_i, (i = 1, 2, \dots, n) \tag{3.3}$$

The averages $\bar{N}_i, (i = 1, 2, \dots, n)$ are the phenomenological variables of the deterministic model. The probability distribution $p(N_i)$ can be estimated by the principle of maximum-entropy estimation [16] which consists of the maximization of the entropy (3.1) with $W(N_i)$ given by (3.2) subject to the condition (3.3) and the normalization condition[15]:

$$\sum_{\{N_i\}} p(N_i) = 1 \tag{3.4}$$

The maximization leads to the Poissons' distribution

$$p(N_i) = \frac{\exp(-\bar{N}_i)(\bar{N}_i)^{N_i}}{N_i!} \tag{3.5}$$

determining the law of probability distribution $p(N_i)$. For ideal gas model of the ecosystem the probability distribution of $N = (N_1, N_2, \dots, N_n)$ is given by

$$P(N) = \prod_{i=1}^n p(N_i) \tag{3.6}$$

or

$$k \ln P(N) = k \ln P(N_1, N_2, \dots, N_n) = k \sum_{i=1}^n [(N_i - \bar{N}_i) - N_i \ln \frac{N_i}{\bar{N}_i}] \tag{3.7}$$

The entropy of the whole multi-component ecosystem is then given by the generalized Boltzmann entropy [14]

$$\begin{aligned} -k \ln P(N_1, N_2, \dots, N_n) &= -k \sum_{i=1}^n [(N_i - \bar{N}_i) - N_i \ln \frac{N_i}{\bar{N}_i}] \\ &= k \sum_{i=1}^n [N_i \ln \frac{N_i}{\bar{N}_i} - (N_i - \bar{N}_i)] \end{aligned} \tag{3.8}$$

where k is the Boltzmann constant proportional to the gas constant R . The right-hand side of (3.8) is proportional to the expression of exergy discussed in the previous section. The left-hand side is the

measure of information obtained from the realization of the macroscopic state $N = (N_1, N_2, \dots, N_n)$ and according to Brillouin's negentropy principle [16], this is equal to the negentropy of the ecosystem which allows the import (or export) of energy, matter and nutrient with the environment of the ecosystem. We thus arrive to the conclusion that the exergy is nothing but the negentropy of the system which according to Jorgensen [3] is one of the definition of exergy [2,3].

Let us now investigate the significance of the probability distribution (3.7) in the study of the stability and evolution of the system. We write the expression (3.7) in the form

$$P(N_1, N_2, \dots, N_n) = \exp\left(-\frac{E_x}{RT}\right) \tag{3.9}$$

where E_x is the exergy given by (2.6). For the study the stability of the thermodynamic equilibrium state $N^* = (N_1^*, N_2^*, \dots, N_n^*)$, let us consider a neighbouring non-equilibrium state $N = (N_1, N_2, \dots, N_n)$ such that

$$N_i = N_i^* + \delta N_i \quad (i = 1, 2, \dots, n) \tag{3.10}$$

where δN_i are the deviations of N_i from the thermodynamic equilibrium value N_i^* . Assuming δN_i to be very small and neglecting higher powers of δN_i , we have

$$E_x = RT + \sum_{i=1}^n \frac{(\delta N_i)^2}{N_i^*} \tag{3.11}$$

Both the exergy-function (2.6) and its local form (3.11) are positive definite and are Lyapunov functions. According to the Lyapunov theorem the criteria of stability of the stationary thermodynamic equilibrium state $(N_1^*, N_2^*, \dots, N_n^*)$ is given by

$$\frac{d}{dt} E_x < 0 \text{ or } \frac{d}{dt} \left[\sum_{i=1}^n \frac{(\delta N_i)^2}{N_i^*} \right] < 0 \tag{3.12}$$

and the criteria of instability of the ecosystem is then given by

$$\frac{d}{dt} E_x > 0 \text{ or } \frac{d}{dt} \left[\sum_{i=1}^n \frac{(\delta N_i)^2}{N_i^*} \right] > 0 \tag{3.13}$$

Let us now study the significance of the inequality (3.12) and (3.13) from the perspective of the law of probability of deviation $(\delta N_1, \delta N_2, \dots, \delta N_n)$

$$P(\delta N_1, \delta N_2, \dots, \delta N_n) = \exp\left[-\sum_{i=1}^n \frac{(\delta N_i)^2}{N_i^*}\right] \tag{3.14}$$

which is a normal distribution. From the probabilistic point of view the stability of the stationary state N^* implies the increasing of the probability (3.14) of finding the system near the stationary state N^* . On the other hand, the instability of the stationary state N^* implies the decreasing of the probability (3.14) of finding the system near the stationary state N^* . The decreasing of the probability (3.14) with

time which results from the criteria of instability (3.13) of the stationary state N^* implies the system evolving out of the domain of attraction of the stationary state N^* . Since the evolution is through the process of successive instabilities [8,9], we can set the criteria of evolution of the ecosystem as the decreasing of the probability (3.14) with time

$$\frac{d}{dt} P(\delta N) < 0 \quad (3.15)$$

or equivalently the increasing of the exergy with time

$$\frac{dE_x}{dt} > 0 \quad (3.16)$$

which is the well-known Jorgensen's principle of increasing of exergy for the ecosystem evolution [17]. According to (3.8) the increasing of exergy with time implies the increasing of information or negentropy which allows the import of energy, matter and nutrient from the environment. The increase of negentropy (or equivalently the decrease of entropy) is a characteristic property of organization. The increase of organization is the characteristic property of evolution of the ecosystem [8]. The validity of the increasing law of exergy for ecosystem is limited to the vicinity of thermodynamic equilibrium state only. However, it is assumed that this statement is true only along the whole system trajectory in course of the evolution from the thermodynamic equilibrium, which is identified as some prebiological situation to the current state [2,3].

Conclusion

In conclusion let us study the parallelism between two vital concepts of thermodynamics and their implication in the study of ecosystems. The first is the concept of entropy-production which is a measure of irreversibility of natural processes. The second is the exergy which is closely related to the irreversibility and takes into account of both quality and quantity of energy and represents the maximum available work that can be extracted from a system and its environment when the system passes from a given non-equilibrium state to the state of thermodynamic equilibrium with its environment. It is also a measure of the departure of the state of the system from its reference environment. Unlike the entropy that is produced by irreversibility of the processes, exergy is always destroyed by irreversibility [3]. We have seen in section (2) that the entropy-produced by irreversibility, that is, the entropy-production $\Delta_i S$ is proportional to the amount of exergy destroyed by irreversibility (exergy destruction):

$$|dE_x| = T\Delta_i S \quad (4.1)$$

where T is the temperature of the environment. Both the concepts of entropy and exergy have significant importance in ecology and lead to some significant results of the thermodynamics of ecosystems [2,3]. One of the significant results is the parallelism between the concepts of entropy principle and exergy principle for evolution of living systems from organisms to ecosystems [18].

In the study of parallelism between the concepts of entropy (or entropy-production) and exergy, let us point out some disagreements between them. The first difference between them arises in the definition of the measures of entropy and exergy. From the definition of exergy we see that it is dependent on the state of the total system (system + reservoir) and not dependent entirely on the state of the system. Exergy is therefore not a state variable, where as the entropy is a state variable. All processes, in reality, are irreversible, which means that the exergy is lost and entropy is produced. The loss of exergy and production of entropy are two different descriptions of the same reality, namely that all processes are irreversible. The relation between these two descriptions has been expressed nicely by the mathematical

expression (4.1). From the point of view of utility, the exergy is more useful to apply than the entropy to describe the irreversibility as it (exergy) has the same unit as energy and is an energy form. The definition of entropy is more difficult to reduce to the concepts associated with our usual description of reality [2]. In addition, entropy is not clearly defined for system far from equilibrium, particularly for living systems [2]. Finally, we note that the self-organizing capacities of systems are strongly dependent on temperature [2]. Exergy takes temperature into consideration as the definition shows, while the entropy doesn't [2].

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