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Boltzmann Entropy: Generalization and Applications

C.G. CHAKRABARTI[1] and KAJAL DE[2]
[1] *Department of Applied Mathematics, University of Calcutta, Calcutta, India;* [2] *Department of Applied Mathematics, Vidyasagar University, Midnapore, W.B., India*

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Abstract. The object of the paper is to generalize Boltzmann entropy to take account of the subjective nature of a system. The generalized entropy or relative entropy so obtained has been applied to an ecological system leading to some interesting new results in violation of existing physical laws. The entropy was further developed to derive a generalized macroscopic measure of relative entropy which plays a significant role in the study of stability and evolution of ecological and chemical reaction systems.

Key words: Boltzmann entropy, Subjectivity, Relative entropy, Equipartition law, Statistical Equilibrium, Ecological systems

1. Introduction

The concept of entropy is fundamental in thermodynamics. In statistical mechanics, it is crucial in the understanding of the macroscopic behaviour of a system within the molecular disorder or chaos of the system. Boltzmann was the first to give statistical measure of this molecular disorder. This measure known as Boltzmann entropy is the basis of all entropy concepts in modern science. The development of this entropy is not closed but is open, awaiting further study and characterization, generalization and new applications. The object of the present paper is to generalize Boltzmann entropy in the perspective of the subjective nature of a system and to study its application in a field other than physics. The organization of the paper is as follows. The second section deals with the generalization of Boltzmann entropy to take account of the subjectivity of the selection of states. This has led to a measure of relative entropy or information. In the third section, this generalized entropy (or relative information) has been applied to the study of the statistical equilibrium of a system, in particular an ecological system, which has led to some new results in violation of existing physical laws. In section four, we provide the derivation of a generalized measure of entropy or information which is significant in the study of the stability and evolution of some ecological and chemical reaction systems.

2. Generalized Boltzmann Entropy and Subjective Entropy

Let us consider a classical system consisting of N elements (molecules, cells, organisms etc.) classified into n classes (energy-states, species, etc.). Let N_i $(i = 1, 2, \ldots, n)$ be the occupation numbers of the ith class. The macrostate of the system is given by the set of occupation numbers $A_n = \{N_1, N_2, \ldots, N_n\}$. The statistical weight or thermodynamic probability of the macrostate A_n is given by

$$W(A_n) = \frac{N!}{\prod_{i=1}^{n} N_i!}, \tag{2.1}$$

which is the total number of microscopic states or complexions compatible with the constraints of the system. The distribution of the elements among the different classes possesses a great deal of disorder or chaos. The statistical measure of this disorder is given by Boltzmann entropy [2]

$$S = K \ln W(A_n), \tag{2.2}$$

where K is a constant and depends on the unit of measurement of entropy. For thermodynamic system K is the Boltzmann constant. An axiomatic derivation of this entropy was given by the authors recently [3]. For large N_i $(i = 1, 2, \ldots, n)$, the Boltzmann entropy (2.2) with $W(A_n)$ given by (2.1) reduces to the form

$$S = -KN \sum_i p_i \ln p_i, \tag{2.3}$$

where $p_i = \frac{N_i}{N}$ is te relative frequency of the ith class and for large n, is equal to the probability that an element lies in the ith class. The expression

$$H(p_1, p_2, \ldots, p_n) = -K \sum_i p_i \ln p_i \tag{2.4}$$

appearing in the r.h.s. of (2.3) is the Shannon entropy and is the basis of the information-theoretic foundation of statistical mechanics initiated by Jaynes [4]. The statistical equilibrium of the system, which corresponds to the maximum value of the entropy (2.2) or corresponds to the maximum of the thermodynamic probability $W(A_n)$, is subject to the given constraints. Now, according to Boltzmann and Planck, the statistical equilibrium of a system is defined as the most probable state of the system. But the thermodynamic probability given by (2.1) is not a probability at all, it is an integer and in fact, for classical systems it is the co-efficient of a multinomial distribution, namely, the probability of the set of occupation numbers $A_n = \{N_1, N_2, \ldots, N_n\}$ given by [5]

$$P(A_n) = P(N_1, N_2, \ldots, N_n) = \frac{N!}{\prod_{i=1}^{n} N_i!} \prod_{i=1}^{n} (p_1^0)^{N_i}, \tag{2.5}$$

where p_i^0 $(i = 1, 2, \ldots, n)$ is the 'a priori' probability that an element lies in the i-th class. In order to remove this confusion about the definition of statistical equilibrium and to make the concept of statistical equilibrium equivalent to the concept of maximum entropy, let us define a generalized entropy which we call the generalized Boltzmann entropy by

$$S_g = K \ln P(A_n) = K \ln P(N_1, N_2, \ldots, N_n). \tag{2.6}$$

Again, for large N_i $(i = 1, 2, \ldots, n)$ using the Stirling approximation, we can reduce (2.6) to the form of a relative entropy

$$S_g = -NK \sum_{i=1}^{n} p_i \ln \frac{p_i}{p_i^0}. \tag{2.7}$$

The expression (2.7), except for the multiplicative constant $(-NK)$, is the Kullback-Leibler discrimination information between the probability distributions $\{p_i\}$ and $\{p_i^0\}$ [6]. In the case of maximally non-committed prior $p_i^0 = \frac{1}{n}$ $(i = 1, 2, \ldots, n)$, it reduces to the form of Shannon entropy.

The generalized Boltzmann entropy or relative entropy (2.7) is a special case of subjective entropy introduced by Jumarie [7], for it can be written in the form

$$S_g = -NK \sum_{i=1}^{n} p_i \ln p_i + NK \sum_{i=1}^{n} p_i \ln p_i^0. \tag{2.8}$$

The subjectivity results from the second term of the r.h.s. of (2.8) which depends on the subjective character of the prior probability distribution $\{p_i^0\}$. The presence of the prior probability p_i^0 or the subjective term in the measure of entropy, can give rise to some interesting results. In the next section, we study the significance of this subjectivity in the context of an ecological system.

3. Maximum Entropy and Statistical Equilibrium

The statistical equilibrium of the system, according to the Boltzmann and Planck definition, corresponds to the maximization of the probability, $P(A_n)$, or equivalently (2.6) or (2.7), subject to the constraints of a fixed number of molecules (or organisms) N and fixed energy E:

$$\sum_{i=1}^{n} N_i = N, \ \ \sum_{i=1}^{n} N_i E_i = E, \tag{3.1}$$

where E_i is the energy of a single molecule (or organism) of the ith energy state or class. The maximization leads to the distribution,

$$p_i = \frac{N_i}{N} = p_i^0 e^{-\beta E_i} / Z(\beta), \tag{3.2}$$

where

$$Z(\beta) = \sum_{i=1}^{n} p_i^0 e^{-\beta E_i} \tag{3.3}$$

is the normalization factor. Now how is the ‘a priori’ probability p_i^0 determined? No state is more probable than another. It is reasonable to assume that all the a priori probabilities p_i^0 are equal to one another, so that $p_i^0 = \frac{1}{n}$ $(i = 1, \dots, n)$. This is the principle of insufficient knowledge. Then the most probable distribution reduces to the form

$$\hat{p}_i = \frac{1}{n} e^{-\beta E_i} / Z(\beta), \tag{3.4}$$

which is the famous Boltzmann distribution in statistical mechanics. With ‘a priori’ probability $\left(\frac{1}{n}\right)$, the entropy corresponding to this most probable state of statistical equilibrium is

$$\begin{aligned}\hat{S}_{\text{equil}} &= -KN \sum_i \hat{p}_i \ln \hat{p}_i \\ &= NK[\ln n + (\beta E + \ln Z(\beta))].\end{aligned} \tag{2.5}$$

With a priori probability p_i^0, the entropy of the most probable state of statistical equilibrium is

$$\begin{aligned}S^0_{\text{equil}} &= -NK \sum_i p_i \ln p_i \\ &= -NK \sum_i p_i^0 \ln p_i^0 + NK(\beta E + \ln Z(\beta)).\end{aligned} \tag{2.6}$$

Since

$$\ln n \geq -\sum_{i=1}^{n} p_i^0 \ln p_i^0, \tag{2.7}$$

we have

$$\hat{S}_{\text{equil}} \geq S^0_{\text{equil}}, \tag{2.8}$$

implying that the statistical equilibrium with ‘a priori’ probability p_i^0 may not correspond to the maximum value of the entropy and hence to the maximum disorder of the system [8].

For an example, let us consider an ecological system of population consisting of N animals of a given species. The animals can be divided into different states k. The states can be resting, hunting, hiding, etc. corresponding to different activities. Let N_k be the number of animals in the state k at time t and p_k^0 be the ‘a priori’ probability that an animal is in the state k. Let E_k be the energy spent per unit time by an animal in the activity k. Let the whole population N $(N = \sum_k N_k)$ use a constant energy E, say, per unit time to realize these activities. Thus we have as before the constraints

$$\sum_k N_k E_k = E \text{ (Constant)}$$

$$\sum_k N_k = N \text{ (Constant).} \tag{3.9}$$

The most probable distribution of animals for statistical equilibrium is given, as before, by

$$p_k = \frac{N_k}{N} = p_k^0 e^{-\beta E_k}/Z(\beta),$$

or,

$$N_k = N p_k^0 e^{-\beta E_k}/Z(\beta). \tag{3.10}$$

In view of the inequality (2.8) we see that the most probable state of statistical equilibrium with a priori probability p_k^0 does not correspond to the maximum entropy or maximum disorder of the system. This corresponds to the non-uniform distribution of energy in violation of the law of equipartition of energy in classical statistics [8], and is due to the presence of the a priori probability p_i^0 of the selection of states, i.e., the states of hunting, hiding, resting etc. The animals, in fact, select their states of activity according to their needs and wishes. The selection of states, therefore, is of subjective nature depending entirely on the animals. The above example illustrates how subjectivity arises in an ecological system and how subjectivity in the states of a system makes things complicated in complete violation of an existing physical law [9].

4. Generalized Relative Entropy and Lyapunov Function

In section two, we saw that for large N, Boltzmann entropy can be written in the form (2.3). Returning to the occupation numbers N_i, the entropy (2.3) can be expressed as

$$S = -K \sum_{i=1}^{n} N_i \ln\left(\frac{N_i}{N}\right) = -K \sum_{i+1}^{n} N_i \ln N_i + KN \ln N. \tag{4.1}$$

The expression (4.1) has, however, a drawback. It does not satisfy the additivity or extensive property of the Boltzmann entropy, which is essential for the axiomatic derivation of the form of the Boltzmann entropy [3]. This, fallacy, is in fact, due to Gibbs' paradox [10]. To remove this fallacy, we must subtract $K \ln N! \approx KN(\ln N - 1)$ from the r.h.s. of (4.1). This leads to the correct expression of Boltzmann entropy for classical systems [10]

$$S = -K \sum_{i=1}^{n} N_i \ln N_i + KN, \tag{4.2}$$

which evidently satisfies the additivity property. The subtraction of the term $\ln N!$ from (4.1) is equivalent to omitting the term $N!$ in the expression (2.1) for the statistical weight. So the correct expression of statistical weight for classical systems should be:

$$W(A_n) = \prod_{i=1}^{n} \left(\frac{1}{N_i!}\right). \tag{4.3}$$

With this expression for statistical weight, let us now turn back to the expression for the probability of macrostate (2.5) and the determination of the 'a priori' probability by the statistical method of maximum-likelihood estimation. The whole system can be considered as an aggregate of n independent subsystems, each subsystem consisting of N_i elements. Each subsystem is characterized by the probability $P(N_i)$ of the occupation number N_i given by:

$$P(N_i) = CW(N_i)(p_i^0)^{N_i}, \tag{4.4}$$

where $W(N_i)$ is the statistical weight of N_i, and C is a constant of normalization. The statistical weight $W(N_i)$ for a classical system consistent with (4.3) is given by

$$W(N_i) = \frac{1}{N_i!}. \tag{4.5}$$

Then the normalization condition $\sum_{N_i} P(N_i) = 1$ gives

$$C \sum_{N_i=0}^{\infty} \frac{{P_i^0}^{N_i}}{N_i!} = 1 \text{ giving } C = e^{-p_i^0}, \tag{4.6}$$

so that the probability $P(N_i)$ becomes

$$P(N_i) = \frac{e^{-p_i^0} {p_i^0}^{N_i}}{N_i!}, \tag{4.7}$$

which is a Poisson distribution with parameter p_i^0. The main problem is to determine p_i^0 and for this we adopt the principle of maximum-likelihood estimation [11]. We take a series of observations $N_{i_1}, N_{i_2}, \ldots, N_{i_r}$, so the likelihood function L is given by

$$L(N_{i_1}, N_{i_2}, \ldots, N_{i_r}) = \frac{e^{-p_i^0 r}(p_i^0)^{\bar{N}_i r}}{N_{i_1}!\, N_{i_2}! \ldots N_{i_r}!}, \tag{4.8}$$

where

$$\bar{N_i} = \frac{1}{r}(N_{i_1} + N_{i_2} + \ldots + N_{i_r}) \tag{4.9}$$

is the sample average. The maximum likelihood estimate of p_i^0 is given by

$$\frac{\delta}{\delta p_i^0} \ln L = 0 \text{ leading to } p_i^0 = \bar{N}_i. \tag{4.10}$$

The probability $P(N_i)$ then becomes

$$P(N_i) = \frac{e^{-\bar{N}_i(\bar{N}_i)^{N_i}}}{N_i!}, \tag{4.11}$$

and the probability of the macrostate $A_n = \{N_1, N_2, \ldots, N_n\}$ is then given by

$$P(A_n) = P(N_1, \ldots, N_n) = \prod_{i=1}^{n} \frac{e^{-\bar{N}_i}(\bar{N}_i)^{N_i}}{N_i!}. \tag{4.12}$$

Therefore, the generalized Boltzmann entropy S_g takes the form

$$\begin{aligned} S_g &= K \ln P(A_n) \\ &= K \sum_{i=1}^{n} \left[(N_i - \bar{N}_i) - N_i \ln \frac{N_i}{\bar{N}_i} \right], \end{aligned} \tag{4.13}$$

which can be considered as a generalized measure of relative entropy or directed divergence between the two non-probability distribution $\{N_i\}$ and $\{\bar{N}_i\}$ [12]. The probability distribution then reduces to the well-known form of relative entropy or $K - L$ discrimination information or directed divergence [6]. The expression (4.13) which is non-negative and equal to zero for $N_i = \bar{N}_i$ for every i is taken as the Lyapunov function in the dynamical study of stability of many ecological systems [13]. It is also the expression of entropy-production in the non-equilibrium thermodynamic model of chemical systems developed by Ishida [14] and that of ecosystems developed by Chakrabarti et al. [15, 16].

5. Conclusion

The Boltzmann entropy has been modified to include subjectivity in the description of a system by introducing ‘a priori’ probabilities. This ‘subjectivity’ is avoided in statistical mechanics by the hypothesis of equal a priori probabilities [5]. But this is not so in other branches of science. For example, in ecological systems where the states of activity of an animal such as hiding, resting, hunting etc. are selective in nature. This has led to violation of some existing physical laws, for example, the equipartition of energy in classical statistics, the equivalence of statistical equilibrium with maximum disorder etc. [8].

The maximum-likelihood estimation of the a priori probabilities p_i^0 led to a generalized measure of relative entropy [12]. If in this generalized measure, we interpret $\bar{N}$ as the stationary value of N (it is justified for large samples), the generalized relative entropy measure can serve as the Lyapunov function in dynamical modelling and as the expression of entropy production in the non-equilibrium thermodynamic modelling of systems. In both the cases, it can be used to study the stability of the system under consideration. Ishida et al. [14] derived this expression in an ad hoc manner by using chemical kinetic equations and in [15] it was derived on the basis of the Lotka-Volterra model equations of ecosystems. The present statistical derivation is, however, independent of any model equations or systems. Its significance in the context of a non-equilibrium thermodynamic theory of stability and evolution of an ecosystem has been studied earlier [15].

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Author for correspondence: C. G. Chakrabarti, Department of Applied Mathematics, University of Calcutta, Calcutta 700 009, India
Phone: +91 33 350–8386