ABSTRACT

For a dynamical system far from equilibrium, one has to deal with empirical probabilities defined through time–averages, and the main problem is then how to formulate an appropriate statistical thermodynamics. The common answer is that the standard functional expression of Boltzmann–Gibbs for the entropy should be used, the empirical probabilities being substituted for the Gibbs measure. Other functional expressions have been suggested, but apparently with no clear mechanical foundation. Here it is shown how a natural extension of the original procedure employed by Gibbs and Khinchin in defining entropy, with the only proviso of using the empirical probabilities, leads for the entropy to a functional expression which is in general different from that of Boltzmann–Gibbs. In particular, the Gibbs entropy is recovered for empirical probabilities of Poisson type, while the Tsallis entropies are recovered for a deformation of the Poisson distribution.
1 Introduction

Classical equilibrium statistical mechanics is a well established subject. One deals with a dynamical system defined by a Hamiltonian function $H$ on a phase space $\mathcal{M}$, which is provided with a suitable probability measure (typically Lebesgue measure). Having fixed a value $U$ of the mean energy, one then correspondingly defines a conditional probability (the Gibbs measure) on $\mathcal{M}$. To obtain statistical thermodynamics, the classical procedure of Gibbs and Khinchin (see [1]) consists first of all in identifying the external work $\delta W$ as $\delta W = \langle \partial_\kappa H \rangle d\kappa$, where $\langle \cdot \rangle$ denotes average with respect to Gibbs measure, and the Hamiltonian has been assumed to depend on an external parameter $\kappa$. A corresponding expression for the exchanged heat $\delta Q$ is thus obtained, as $\delta Q = dU - \delta W$, and this finally allows to introduce entropy in the standard thermodynamic way.

However one often deals with situations in which the relevant probability measure is different from that of Gibbs. Typically this occurs when the probability is defined dynamically in terms of time–averages (sojourn times) and the final time is not long enough for equilibrium to have been attained (statistical mechanics far from equilibrium). In such a case, following Poincaré, Boltzmann and Einstein one can assume that the expectations should be computed in terms of time–averages.

The problem is then to determine which is the correct expression for the thermodynamic functions in such a situation, and for this it is sufficient to provide an expression for the entropy. Many people accept the thesis that entropy should be defined by the classical formula of Gibbs with the only proviso that the empirical probabilities (time–averages) should be substituted for the Gibbs measure. Other people, particularly Tsallis, suggest instead that different formulæ should be used, but a mechanical foundation for such formulæ is apparently lacking.

In the present paper we show how the standard procedure to define entropy recalled above can be implemented also if, in the expression for the external work, the averaging is performed through the empirical probabilities rather than through Gibbs measure. In particular, the standard Gibbs entropy is obtained for empirical probabilities of Poisson type, while the Tsallis entropies are recovered for a deformation of the Poisson distribution. The implementation of the Gibbs–Khinchin procedure requires however to previously define a suitable mathematical setting for dealing with the empirical probabilities. This is dealt with in the first two sections. The thermodynamics is then developed, and the two cases leading to the Gibbs and the Tsallis distributions are finally considered. Some open problems are also mentioned. The style of the paper will be quite informal, with no striving for strict mathematical rigour.
2 A priori probability

Suppose one has a map \( \phi : \mathcal{M} \rightarrow \mathcal{M} \) (for example the time–flow of an autonomous Hamiltonian system at time \( \Delta t \)) in a given phase space \( \mathcal{M} \), and we are interested in computing time–averages of a dynamical variable \( A(x) \) (a real function on \( \mathcal{M} \)):

\[
\bar{A}(x_0) \equiv \frac{1}{N} \sum_{n=1}^{N} A(x_n) \quad \text{for} \quad N \gg 1,
\]

the sequence \( \{x_n\} \) being defined by the recurrence \( x_{n+1} = \phi(x_n) \). The number \( N \) thus plays the role of the “final” time, and since now on will be thought of as a fixed parameter. One can divide the space \( \mathcal{M} \) into a large number \( K \) of disjoint cells \( Z_j \) (such that \( \mathcal{M} = \bigcup Z_j \)), and one has then

\[
\bar{A}(x_0) \simeq \sum_{j=1}^{K} A_j \frac{n_j}{N},
\]

where \( A_j \) is the value of \( A \) in a point \( x \in Z_j \), and \( n_j \) is the number of times the sequence \( \{x_n\} \) visits \( Z_j \). It is clear that \( n_j \) depends on \( x_0 \) so that, if a certain probability distribution is assigned for the initial data \( x_0 \), correspondingly \( n_j \) turns out to be a random variable with a certain distribution function \( F_j(n) \), which will depend both on the dynamics (i.e. on the map \( \phi \)) and on the distribution of the initial data. So one can speak in general of the “a priori probability \( P \) that the cell \( Z_j \) will be visited a number of times \( n_j \leq n \):”

\[
P(n_j \leq n) = F_j(n).
\]

In the following, in order to simplify the discussion, it will be supposed that such a probability does not depend on the cell \( Z_j \) (i.e. \( F_j(n) = F(n) \forall j \)). The general case can also be easily dealt with. With an abuse of notation we will denote by \( F(n_j) \) the probability that the cell \( Z_j \) is visited a number of times \( \leq n_j \), following the common attitude of using the same letter both for a random variable and for its value.

A central point in the discussion is that the time–average \( \bar{A}(x_0) \) is itself a random variable, so that it is meaningful to consider its expectation. Denoting by \( < \cdot > \) expectation with respect to the a priori distribution, one has then

\[
< \bar{A} > = \frac{1}{N} \sum_{j=1}^{K} A_j < n_j >.
\]

A step forward is made if one supposes that the expectation of \( n_j \) can be computed by a formalism analogous to the Grand Canonical one, i.e. if one introduces the
Hypotese 1 The quantities $n_j$ are independent random variables, conditioned by $\sum n_j = N$.

Using this hypothesis, the expectation of $\bar{A}$ can be computed as

$$
< \bar{A} > = \frac{1}{N} \sum_j A_j < n_j > = \frac{1}{N} \sum_j \int \ldots \int \frac{n_j dF(n_1) \ldots dF(n_K)}{\int \ldots \int n_1 = N \sum_j n_j dF(n_1) \ldots dF(n_K)}
$$

In particular, introducing the function

$$
Z(\lambda, A) \overset{\text{def}}{=} \int \ldots \int \frac{e^{-\lambda \sum_j n_j A_j} dF(n_1) \ldots dF(n_K)}{\sum n_j = N},
$$

which generates the moments of the random variable $A$, one obtains

$$
< \bar{A} > = -\frac{1}{N} \theta_\lambda \log Z(\lambda, A) \Big|_{\lambda = 0}.
$$

3 Conditional Probability and Large Deviations

Usually in statistical thermodynamics one does not deal directly with the a priori probability, because it is generally assumed that the time-average of a certain macroscopic quantity, typically the total energy, has a given value, which should play the role of an independent variable. So we consider the total energy, which we now denote by $\varepsilon$, and its time-average $\bar{\varepsilon} = 1/N \sum_j \varepsilon_j n_j$, and we impose on the numbers $n_1, \ldots, n_K$ the condition

$$
\frac{1}{N} \sum_{j=1}^K \varepsilon_j n_j = U = \text{const}.
$$

Actually in such a way one meets with a large deviation problem, because one usually also assumes that one has

$$
U \neq < \bar{\varepsilon} > = \frac{1}{N} \sum_{j=1}^K \varepsilon_j < n_j >,
$$

and furthermore that $U - < \bar{\varepsilon} >$ is large, against the law of large numbers. One is thus in an extremely unlikely situation, where the information on the value $U$ of $\bar{\varepsilon}$ turns out to have a great relevance, by conditioning the expectations of the other quantities of interest. The problem we discuss in the rest of the present section is indeed how to compute such a conditional probability, or a posteriori probability, as it is also called.
Using the tool of the moment function, the a posteriori expectation of $\bar{A}$, denoted by $<\bar{A}>_U$, is given by

$$<\bar{A}>_U = -\frac{1}{N}\partial_\lambda \log Z(\lambda, A, U) \bigg|_{\lambda=0}, \quad (4)$$

where the moment function $Z$ is defined by

$$Z(\lambda, A, U) \overset{\text{def}}{=} \int dA \exp(-\lambda A) \int \cdots \int dF(n_1) \cdots dF(n_K)$$

$$\delta(A - \frac{1}{N}\sum A_j n_j) \delta(U - \frac{1}{N}\sum \varepsilon_j n_j) \delta(N - \sum n_j), \quad (5)$$

$\delta(x)$ being the usual Dirac’s function. Here, use was made of the familiar formula for the conditional probability, namely the formula $P(A|B) = P(A \cap B)/P(B)$, where the event $(B)$ consists in having fixed the time–average of the energy, $\bar{\varepsilon} = U$.

To compute the moment function we use the familiar representation for the Dirac’s function, i.e. $\int_{-L}^{L} dk \exp(ikx) \to \delta(x)$ as $L \to \infty$. One has then

$$Z(\lambda, A, U) = \lim_{L \to +\infty} \int_{-L}^{L} d k_1 \int_{-L}^{L} d k_2 \int dA \exp(-\lambda A)$$

$$\int \cdots \int dF(n_1) \cdots dF(n_K) \exp \left( i(U - \frac{1}{N}\sum \varepsilon_j n_j) k_1 + i(N - \sum n_j) k_2 \right)$$

$$= \lim_{L \to +\infty} \int_{-L}^{L} d k_1 \int_{-L}^{L} d k_2 \exp(ik_1 U + ik_2 N)$$

$$\int \cdots \int dF(n_1) \cdots dF(n_K) \prod_j \exp \left( -n_j \frac{\lambda A_j}{N} - \frac{\varepsilon_j k_1}{N} + i k_2 \right).$$

Notice that in the last integral there appears the Laplace transform of the distribution function $F(n)$. Now we make the following

**Hypotesis 2** Defining $\chi(z)$ by

$$\int_{0}^{+\infty} \exp(-zn)dF(n) = \exp(\chi(z)),$$

we suppose that $\chi(z)$ is analytic in the half plane $\Re z > 0$ (this is true if the random variables $n_j$ are supposed to be infinitely divisible).
Then one has

\[ Z(\lambda, A, U) = \lim_{L \to +\infty} \int_{-L}^{L} d k_1 \int_{-L}^{L} d k_2 \exp \left( i k_1 U + i k_2 N + \sum_j \chi \left( \frac{\lambda A_j}{N} + i \frac{\varepsilon_j k_1}{N} + i k_2 \right) \right). \]  

(6)

An asymptotic expression for the integral (6) can be given through the steepest descent method. One has to find the values of \( k_1 \) and \( k_2 \) which satisfy the system

\[
\begin{align*}
U &= - \frac{1}{N} \sum_j \varepsilon_j \chi' \left( \frac{\lambda A_j}{N} + i \frac{\varepsilon_j k_1}{N} + i k_2 \right) \\
N &= - \sum_j \chi' \left( \frac{\lambda A_j}{N} + i \frac{\varepsilon_j k_1}{N} + i k_2 \right). 
\end{align*}
\]  

(7)

One can show that such values exist provided one makes the further assumption (to which we plan to come back in the future)

\[ U \leq < \varepsilon >. \]

It then turns out that such values are imaginary, so we denote them by \( ik_1 = \theta \) and \( ik_2 = \alpha \). In addition, one also has to compute the determinant \( \det H(\theta, \alpha) \) of the second derivatives, which gives

\[
\det H(\theta, \alpha) = \sum_{j,k} \frac{\varepsilon_j^2 - \varepsilon_k \varepsilon_k}{N^2} \chi'' \left( \frac{\lambda A_j}{N} + \theta \varepsilon_j + \alpha \right) \chi'' \left( \frac{\lambda A_k}{N} + \theta \varepsilon_k + \alpha \right). 
\]  

(8)

One has thus

\[ Z(\lambda, A, U) \simeq \exp \left( \theta U + \alpha N + \sum_j \chi' \left( \frac{\lambda A_j}{N} + \theta \varepsilon_j + \alpha \right) \right) \sqrt{\det H(\theta, \alpha)}. \]  

(9)

Obviously, to obtain bounds on the errors, one should give an estimate of the quantity \( \det H(\theta, \alpha) \), but this depends on the functions \( \varepsilon \) and \( \chi(z) \). From now on, we suppose that the denominator in (9) can be neglected in the computations of the expectations. This will be checked to be true, in all the examples to be considered below. Thus, for the expectation one has the formula

\[
< A >_U = - \partial_\lambda \log Z(\lambda, A, U)|_{\lambda=0} \\
= - \left( \partial_\lambda \theta U + \partial_\lambda \alpha N + \sum_j \chi' \left( \frac{\theta \varepsilon_j}{N} + \alpha \right) \left( \frac{A_j}{N} + \partial_\lambda \theta \varepsilon_j + \partial_\lambda \alpha \right) \right)|_{\lambda=0}.
\]
which finally, using (7), becomes

\[
< \bar{A} >_U = -\frac{1}{N} \sum_j A_j \chi' \left( \frac{\theta \varepsilon_j}{N} + \alpha \right). \tag{10}
\]

With this result, the form of the expressions (7) and (10) shows that the quantity \(-\chi'(\varepsilon_j \theta/N + \alpha)\) plays the role of the mean number of times the cell \(Z_j\) is visited. Indeed, in terms of the quantities

\[
\bar{\nu}_j \overset{\text{def}}{=} -\chi'(\varepsilon_j \theta/N + \alpha), \tag{11}
\]

such relations can be written as \(N = \sum \bar{\nu}_j, U = \sum \varepsilon_j \bar{\nu}_j/N\) and \(< \bar{A} >_U = \sum A_j \bar{\nu}_j/N\). The quantity \(\bar{\nu}_j\) may be called the mean occupation number of cell \(Z_j\).

4 The Thermodynamics

The expression (10) solves the problem of computing the conditional expectation, but one can ask for the meanings of the two quantities \(\theta\) and \(\alpha\). Let us consider the problem of \(\theta\). To this end it is convenient to introduce as an independent variable, instead of \(z_j\), the quantity \(\nu_j = -\chi'(z_j)\), and this naturally leads to introducing in place of \(\chi\) its Legendre transform \(h\) defined as usual by

\[
h(\nu_j) = (\nu_j z_j + \chi(z_j)) \bigg|_{\nu_j = -\chi'(z_j)}. \tag{13}
\]

Notice that, while \(\bar{\nu}_j\) has the meaning of a mean occupation number (conditioned on \(U\)), the quantity \(\nu_j\) just plays the role of a parameter, in the same sense as \(z_j\) does. In particular, the quantities \(\nu_j\) do not need satisfy any condition related to normalization, or the fixing of an energy value. One has then

**Proposition 1** The values \(\bar{\nu}_j = -\chi'(\varepsilon_j \theta/N + \alpha), i = 1, \ldots , K,\) correspond to a maximum of the function

\[
S(\nu_1, \ldots , \nu_K) \overset{\text{def}}{=} \sum_{j=1}^K h(\nu_j), \tag{12}
\]

constrained to the surfaces \(\sum \nu_j = N\) and \(\sum \varepsilon_j \nu_j/N = U\).

**Proof.** One simply considers the function \(G \overset{\text{def}}{=} S - (\theta/N) \sum \varepsilon_j \nu_j - \alpha \sum \nu_j\), and from \(\partial_{\nu_j} G = 0\) one gets

\[
h'(\bar{\nu}_j) = \frac{\theta \varepsilon_j}{N} + \alpha. \tag{13}
\]
But now, from the Legendre duality, one has
\[ h'(\bar{\nu}_j) = \frac{\theta \varepsilon_j}{N} + \alpha \quad \iff \quad \bar{\nu}_j = -\chi' \left( \frac{\theta \varepsilon_j}{N} + \alpha \right), \]
from which the thesis follows. One easily checks that one actually deals with a maximum. Q.E.D.

As a corollary there follows that the maximum of \( S \) (divided by \( N \)) is indeed the thermodynamic entropy, and \( \theta/N \) the inverse temperature, or at least an integrating factor of the exchanged heat. In other terms, the thermodynamic entropy \( S^\text{th}(\theta, \alpha) \) turns out to be given by
\[ S^\text{th}(\theta, \alpha) \overset{\text{def}}{=} \frac{S(\bar{\nu}_1, \ldots, \bar{\nu}_K)}{N}, \]
up to an additive constant.

In fact, suppose now that the values \( \varepsilon_j \) depend on some external parameter, say \( \kappa \). Then \( \partial_{\kappa} \varepsilon_j \) is the reaction force needed to keep the parameter fixed when the system is in cell \( Z_j \) of the phase space, so that the quantity \( \partial_{\kappa} \varepsilon_j \, d \kappa \) is the (instantaneous) work performed on the system when the external parameter is changed by a quantity \( d \kappa \). For the macroscopic work \( \delta W \), namely the expectation of the time–averaged instantaneous work, using relation (10) one then obtains the expression
\[ \delta W = \frac{1}{N} \sum_j \bar{\nu}_j \partial_{\kappa} \varepsilon_j \, d \kappa. \]
By definition, the exchanged heat is then
\[ \delta Q \overset{\text{def}}{=} dU - \delta W = \frac{1}{N} \sum_j \bar{\nu}_j \partial_{\kappa} \varepsilon_j \, d \kappa = \frac{1}{N} \sum_i \varepsilon_j \, d \bar{\nu}_j. \]
On the other hand, from (13) one has \( \varepsilon_j/N = (h'(\bar{\nu}_j) - \alpha)/\theta \), so that one finds
\[ \delta Q = \frac{1}{\theta} \sum_i h'(\bar{\nu}_j) \, d \bar{\nu}_j - \frac{\alpha}{\theta} \sum_j d \bar{\nu}_j = \frac{N}{\theta} \, d S^\text{th}, \]
because in our hypotheses \( N \) is kept constant, so that \( \sum_j d \bar{\nu}_j = 0 \). Concerning the physical meaning of \( \alpha \), we have no clear idea at the moment.
The most natural choice for the distribution function that one might consider is that of Poisson, namely

\[ F(n_j) = \sum_{k \leq n_j} \frac{e^{-p}}{k!} p^k , \]

where \( p \) is a positive parameter. This corresponds to assuming that the successive visits of a given cell are independent events.

The Laplace transform then has the form

\[
\int_0^{+\infty} e^{-nz} \, dF = e^{-p} \sum_{n=0}^{+\infty} \frac{e^{-nz} p^n}{n!} = \exp(pe^{-z} - p) ,
\]

which in particular exhibits the well known fact that the distribution is infinitely divisible. One has thus

\[ \chi(z) = pe^{-z} - p , \]

and

\[ \bar{\nu}_j = -\chi\left(\frac{\theta \varepsilon_j}{N} + \alpha\right) = pe^{-\alpha} e^{-\theta \varepsilon_j/N} . \]

The condition \( \sum \bar{\nu}_j = N \) then gives \( pe^{-\alpha} = N/Z(\beta) \), where \( Z(\beta) \) is the usual canonical partition function, and \( \beta = \theta/N \). Thus, for the mean occupation number one has the usual Gibbs formula

\[ \bar{\nu}_j N = e^{-\beta \varepsilon_j} Z(\beta) . \]

With this result, the value of the denominator in (9) can be computed, and one gets

\[
\sum_{j,l} \frac{\varepsilon_j^2 - \varepsilon_j \varepsilon_l}{N^2} \chi'' \left( \frac{\lambda A_j}{N} + \frac{\theta \varepsilon_j}{N} + \alpha \right) \chi'' \left( \frac{\lambda A_j}{N} + \frac{\theta \varepsilon_j}{N} + \alpha \right) = \]

\[
= \sum_j \frac{\varepsilon_j^2 e^{-(\lambda A_j/N) - \beta \varepsilon_j}}{Z(\beta)} - \left( \sum_j \frac{\varepsilon_j e^{-(\lambda A_j/N) - \beta \varepsilon_j}}{Z(\beta)} \right)^2 ,
\]

a quantity which tends, for \( \lambda \to 0 \), to the familiar expression for the canonical specific heat \( C_V \). So, if the specific heat \( C_V \) is an extensive quantity of the same order of magnitude as \( U \), as usual for the systems dealt with in statistical mechanics, it follows that the steepest descent method gives
the correct answer. In addition, in computing the expectation of $\bar{A}$ the denominator gives a contribution equal to

$$\partial_\lambda \log C_V = \frac{\partial_\lambda C_V}{C_V},$$

which is of order $O(1)$ for quantities $A$ of macroscopic type, and so can be safely ignored.

Coming finally to the computation of the entropy, one first has to compute the quantity $h(\nu) = \nu z + pe^{-z} - p$ using $\nu = pe^{-z}$, i.e. $z = -\log \nu + \log p$, so that one has $h(\nu) = -\nu \log \nu + \nu + \nu \log p - p$. Thus for the entropy one finds the expression

$$S = -\sum_j \nu_j \log \nu_j + N(1 + \log p) - Kp,$$

i.e., up to an additive constant, the classical expression of Boltzmann (or rather the analogous one of Gibbs involving the global phase-space).

6 The infinitely divisible distributions and the Tsallis entropies

The infinitely divisible distributions are characterized according to the following theorem (see the classical handbook [2] of Feller)

**Theorem 1** The function $\exp(\chi(z))$ is the Laplace transform of an infinitely divisible distribution if and only if $\chi(0) = 0$ and $(-1)^n \chi^{(n)}(z) > 0$, $\forall z \in \mathbb{R}^+$ and $\forall n \in \mathbb{N}$.

Perhaps, the simplest choice consists in considering the inverse powers of $z$. Taking into account normalization conditions, one is then naturally led to consider the one–parameter family, parameterized by $\gamma > 0$, which, for any positive constant $p$, is given by

$$\chi(z) = p \left(1 + \frac{z}{\gamma}\right)^{-\gamma} - p.$$  \hspace{1cm} (14)

Notice that it reduces to the Poisson distribution in the limit $\gamma \to +\infty$.

The mean occupation number $\bar{\nu}_j$ is then given, using (11), by

$$\bar{\nu}_j = p \left(1 + \frac{\theta \varepsilon_j}{N\gamma} + \frac{\alpha}{\gamma}\right)^{-\gamma-1}.$$  \hspace{1cm} (15)

Now, it turns out that this coincides, with a suitable relabeling of the parameters, with the Tsallis distribution of index $q$ (see [3]),

$$\bar{\nu}_j = C(1 + \beta_q(q-1)\varepsilon_j)^{\frac{1}{q-1}}.$$
if one sets

\[ \gamma = \frac{1}{q-1} . \]

Notice that, in terms of the parameter \( q \), the one–parameter family (14) can also be written in a form reminiscent of the Poisson distribution, namely

\[ \chi(z) = pe^{-z^q} - p , \]

where \( e^z_q \) is the \( q \) deformation of the exponential introduced by Tsallis, namely

\[ e^z_q = (1 + (1 - q)x)^{1/q} . \]

The fact that the mean occupation number, as a function of energy, is a \( q \)-distribution is due to the fact that the entropy (12) corresponding to distribution (14) essentially coincides with that of Tsallis. In fact, from (14) one has

\[ \nu_j = p \left( 1 + \frac{z_j}{\gamma} \right)^{-\gamma-1} , \]

so that, computing \( z_j \) as a function of \( \nu_j \), one gets

\[ h(\nu_j) = (\gamma + 1)\nu_j^{-\gamma+1} p^{1/\gamma} - \gamma \nu_j - p . \]

Apparently, the entropy \( S = \sum h(\nu_j) \) thus obtained does not have the form of the Tsallis entropy, even if \( \gamma \) is expressed in terms of \( q \) as above. However the coincidence (apart from an inessential multiplicative constant) is obtained if the present entropy is written in terms of the quantities \( p_j^{\#} \equiv p_j / q^{-1/2} \nu_j^{1/2} \) and if the mean energy is computed in terms of “escort” probabilities (see [4]), namely \( p_j^{\#} \), i.e. essentially our \( \bar{\nu}_j \). Indeed, in terms of the variables \( p_j \) and of the parameter \( q \) the present entropy \( S \) reads

\[ S(p_1, \ldots , p_K) = C(q) \frac{\sum_j p_j - \sum_j p_j^q}{q - 1} , \]

where we have introduced the constant \( C(q) \equiv pq^{(q-1)/2} \). This expression differs from that of Tsallis only by a multiplicative constant, so that obviously both entropies produce by maximization the same distribution.

In a such a way the expressions of the Tsallis entropies are recovered. The main difference seems to be that the present procedure, in virtue of its statistical–mechanics foundation, does not require any jumping between probabilities and escort probabilities.
7 Conclusions

We believe we have given a consistent procedure to define a thermodynamic entropy for off–equilibrium situations. A characteristic feature of the present approach is that it follows the same scheme of Gibbs and Khinchin, which consists in finding an integrating factor for the exchanged heat, with no mention of information theory at all. We are well aware however of the fact that another problem remains open, because in general there exist infinitely many integrating factors, so that a further requirement is needed in order to uniquely determine the thermodynamic entropy. This fact was particularly emphasized for example by Ehrenfest and Caratheodory (see [5]). Notice that such a requirement involves the question of the extensivity property of entropy. These interesting problems are left for possible future studies.

Another subject for further study is the dependence of the entropy on the number \( N \) of iterations, i.e. on time.

The second peculiarity of the present approach concerns the essential ingredient through which probability was introduced, namely the probability distribution \( F(n_j) \) for the number of visits of cell \( Z_j \), against the common use of interpreting the numbers \( n_j/N \) themselves somehow as probabilities. It has been shown how thermodynamics turns out to be defined in terms of the function \( \chi(z) \) uniquely associated to the distribution \( F(n_j) \). Notice that the treatment developed here can be easily extended to the nonhomogeneous case, in which the probability distribution \( F \) depends on cell \( Z_j \). In such a case the function \( \chi(z) \) too depends on \( j \) as does the function \( h \). One has then for example \( \bar{\nu}_j = -\chi'_j(\varepsilon_j \theta/N + \alpha) \) and \( S(\nu_1, \ldots, \nu_K) = \sum h_j(\nu_j) \), and everything remains essentially unchanged.

References


