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A Definition of Irreversible Entropy Change by Detailed (Im)balance of a Stochastic Process

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Entropy change δS is defined by the "detailed imbalance" of a stochastic process describing irreversible evolution. The detailed imbalance for a pair of configurations i and j is $\log(p_i^t f_{ij}/p_j^t f_{ji})$, where p_i^t and p_j^t are the probabilities at time t and f_{ij} and f_{ji} are the transition probabilities. This quantity, averaged for all i, j transitions, is equated to δS. The definition facilitates the description of entropy changes for a nonisolated system interacting with its surroundings, δS decomposing into $\delta S_{\text{syst}} - \delta S_{\text{ext}}$. The former, related to $\log(p_i^t/p_j^t)$, is the change in the state entropy of the system; the latter, related to $\log(f_{ij}/f_{ji})$, is the change due to surroundings. Both can be calculated for a stochastic process without recourse to thermodynamic variables. As an example, δS is calculated for a nonlinear diffusion process and is shown to decrease monotonically with the time, conforming with "minimum entropy production." Relationship to other definitions is discussed.

KEY WORDS: Stochastic process; detailed balance; irreversible change; entropy; nonlinear diffusion.

1. INTRODUCTION

Take a macroscopic system to which belongs a set of configurations (microstates) i. The statistical study of the system at equilibrium is with the help of time-independent configurational probabilities p_i. The evolution of probabilities with the time is conveniently described by a stochastic process obeying the master equation; it is reasonable therefore to employ the latter for a statistical study of a macroscopic system not at equilibrium. What quantity of the stochastic process represents the irreversible entropy change, $\delta S > 0$? The common choice$^{(1)}$ is based on Gibbs (coarse-grained) definition of entropy.$^{(2)}$ Recent literature discusses the relative merits of this and

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of alternative definitions.(3–5) Moreover, the calculation of the Gibbs entropy change is for a stochastic process describing an isolated total system. However, the practical description of the time evolution is with the help of a stochastic process which represents the effect of surroundings (e.g., heat bath) on a nonisolated system. Such is the case with the computer Monte Carlo method(6–8) and with theoretical studies based on Glauber's model.(9)

In what follows a different approach is therefore proposed. The irreversible entropy change is defined by a "detailed (im)balance" for pairs of configurations between which the stochastic transitions take place. This definition: (i) reproduces $\delta S \geqslant 0$ and (ii) very conveniently decomposes into two parts, δS_{syst} and $-\delta S_{\text{ext}}$. The first, δS_{syst}, is the entropy change for the nonisolated system; it is equal to a change of the state function $\overline{-\log p}$ associated with the probability distribution. The second, δS_{ext}, is the entropy change due to the surroundings, as represented by the stochastic process transition probabilities. Thus δS_{ext} is equal to $\delta Q/T$ for a system exchanging heat δQ with a bath at T. However, for a stochastic process representing an effect of surroundings which is difficult to define thermodynamically, one can still calculate $-\delta S_{\text{ext}}$ with no difficulty from transition probabilities, as described here and in previous articles.(10) Finally, the reason for relating irreversibility to the detailed imbalance seems to be intuitively more meaningful than the reason for relating it to a coarse-grained probability. As we shall see, the present definition of entropy change is essentially similar to the change of Gibbs entropy, but, in view of (ii) and of its meaningfulness, it seems to be, so to speak, tailored for calculations with the help of a stochastic process.

2. THEORY

Let the macroscopic system be represented by an ensemble of discrete configurations, p_i^t being the probability of configuration i at time t. The evolution of the ensemble, spontaneous or impressed by the surroundings, is described by a Markovian stochastic process. The process effects transitions of the configurations one into another, varying one degree of freedom at a step. Thus a transition corresponds to a flip of one spin for the Ising lattice(7) or to a displacement of one molecule for a model fluid.(6) The process is assumed to be irreducible and aperiodic, viz. to exhibit ergodic convergence.(6,7) The unit time per step is τ, that is, step s corresponds to physical time $t = s\tau$. For pairs of communicating configurations i and j, f_{ij} and f_{ji} are the forward and reverse transition probabilities.

We define the "detailed imbalance" for i and j at time t as follows:

$$X_{ij}^t = \log(p_i^t f_{ij}/p_j^t f_{ji}) \tag{1}$$

The average of this quantity over all $i \to j$ transitions during the time interval from s to $s + 1$ is

$$\overline{X^t} = \sum_i \sum_j p_i^t f_{ij} X_{ij}^t \tag{2}$$

where

$$\sum_j f_{ij} = 1 \qquad \text{(including } i = j\text{)} \tag{3}$$

and

$$\sum_i p_i^t = 1 \tag{4}$$

Our proposal is that $\overline{X^t}$ represents the corresponding rate of change of the thermodynamic entropy. Thus (k being the Boltzmann constant)

$$\delta S/\delta t = k\overline{X^t}/\tau \tag{5}$$

To begin with, we note that the forward $i \to j$ transitions, of frequency $p_i^t f_{ij}$, contribute X_{ij}^t, while the reverse $j \to i$ transitions, of frequency $p_j^t f_{ji}$, contribute

$$X_{ji}^t = \log(p_j^t f_{ji}/p_i^t f_{ij}) = -X_{ij}^t \tag{6}$$

Hence

$$\overline{X^t} = \frac{1}{2} \sum_i \sum_j (p_i^t f_{ij} - p_j^t f_{ji}) \log(p_i^t f_{ij}/p_j^t f_{ji}) \tag{7}$$

But in view of

$$(a - b) \log(a/b) \geqslant 0 \qquad \text{for } a > 0 \text{ and } b > 0 \tag{8}$$

we conclude at once that $\overline{X^t} \geqslant 0$. The limitation here is to initial distributions such that for no configuration is p_i^0 equal to precisely zero, even though for all practical purposes some p_i^0 are effectively null. The form of Eq. (7) implies that $\overline{X^t} = 0$ if, and only if, all communicating i and j obey the equation of detailed balance,

$$p_i^t f_{ij} = p_j^t f_{ji} \tag{9}$$

However, for a Markov process that exhibits convergence toward a time-independent, viz. equilibrium, probability distribution, Eq. (9) constitutes a sufficient condition showing attainment of this equilibrium.(6,7) We conclude therefore

$$\begin{aligned} \overline{X^t} &> 0 \qquad \text{for nonequilibrium} \\ \overline{X^t} &= 0 \qquad \text{at equilibrium} \end{aligned} \tag{10}$$

So far our elected quantity very nicely agrees with the second law. But does it really correspond to δS as calculated from statistical thermodynamics? For that purpose $k\overline{X^t}$ is decomposed as follows [Eqs. (1), (2), and (5)]:

$$k\overline{X^t} = \tau(\delta S/\delta t) = \delta S_{\text{syst}} - \delta S_{\text{ext}} \tag{11}$$

where

$$\delta S_{\text{syst}} = k \sum_i \sum_j p_i^t f_{ij} \log(p_i^t/p_j^t) \tag{12}$$

and

$$-\delta S_{\text{ext}} = k \sum_i \sum_j p_i^t f_{ij} \log(f_{ij}/f_{ji}) \tag{13}$$

To demonstrate that our δS_{syst} agrees with the usual expression of statistical mechanics, namely

$$\delta S^*_{\text{syst}} = -k \sum_i \delta(p_i^t \log p_i^t) = -k\, \delta(\overline{\log p}) \tag{14}$$

we note that

$$\sum_i p_i^t f_{ij} = p_j^{t+\tau} \tag{15}$$

With the help of Eqs. (3) and (15), we rewrite Eq. (12) as follows:

$$\begin{aligned} \delta S_{\text{syst}} &= k \sum_i \sum_j p_i^t f_{ij} (\log p_i^t - \log p_j^t) \\ &= k \sum_i p_i^t \log p_i^t - k \sum_j p_j^{t+\tau} \log p_j^t \\ &= -k \sum_i (\delta p_i^t) \log p_i^t \end{aligned} \tag{16}$$

This is still different from Eq. (14), since $\log p_i^t$ is not varied

$$\delta S_{\text{syst}} - \delta S^*_{\text{syst}} = k \sum_i p_i^t\, \delta(\log p_i^t) \tag{17}$$

However, for a sufficiently small variation per step, the normalization equation (4) leads to

$$\sum_i p_i^t\, \delta(\log p_i^t) \simeq \sum_i p_i^t(\delta p_i^t/p_i^t) = \sum_i \delta p_i^t = 0 \tag{18}$$

We remark that the use of a sufficiently small (infinitesimal) variation δp_i^t in the calculation of δS appears to be accepted without question (see Ref. 1, for example). Still, we would like to deal with a stochastic process the steps of which correspond to some physically meaningful units of a real evolutionary process. In that case the presumed smallness of δp_i^t needs justification.

On the basis of Eqs. (17) and (18) we conclude that the present definition of S_{syst} is equivalent to the conventional definition

$$\delta S_{\text{syst}} = \delta S^*_{\text{syst}} = -k\,\delta(\overline{\log p}) \tag{19}$$

We turn to an evaluation of $-\delta S_{\text{ext}}$, *for the case when the effect of surroundings can be described by thermodynamic variables.* Suppose the system evolves in contact with a reservoir at temperature T. The stochastic process describing the interaction with the reservoir has to reproduce the tendency of the system to ultimately come to equilibrium at T; notably p_i^∞ have to obey the canonical distribution for that temperature (see Ref. 7, for example). Since the equilibrium p_i^∞ obey detailed balance [Eq. (9)], we have

$$f_{ij}/f_{ji} = p_j^\infty/p_i^\infty = \exp(-\Delta H_{ij}/kT) \tag{20}$$

where ΔH_{ij} is the change of enthalpy associated with the transition from an i to j configuration (viz., change of internal energy plus external work if any is required). It follows [Eqs. (13) and (20)] that

$$-\delta S_{\text{ext}} = k\,\overline{\log(f_{ij}/f_{ji})}_t = -(\overline{\Delta H_{ij}})_t/T = -\delta Q/T \tag{21}$$

where δQ is the macroscopic heat given to the system by the surroundings during the time from s to $s+1$. Clearly Eq. (21) is in agreement with thermodynamics. Summing up [Eqs. (11), (19), and (21)], we have

$$k\overline{X^t} = k\,\overline{\log(p_i^t f_{ij}/p_j^t f_{ji})} = \delta S_{\text{syst}} - \delta S_{\text{ext}} = -k\,\delta(\overline{\log p}) - \delta Q/T \tag{22}$$

3. A SIMPLE EXAMPLE

Consider diffusion in a fluid consisting of two types of particles, A and B, which are noninteracting and similar in their kinetic properties. The diffusional exchange is between a system, *assumed to remain homogeneous throughout the process,* and an external reservoir. The concentrations in the system at time t are

$$c_A^t \quad \text{and} \quad c_B^t = 1 - c_A^t \tag{23}$$

Those in the reservoir are

$$c_A^{\text{ext}} \quad \text{and} \quad c_B^{\text{ext}} = 1 - c_B^{\text{ext}} \tag{24}$$

The $A \rightleftarrows B$ exchange of the system with the reservoir is described by a stochastic process, exchanging one particle at a time, with the transition probabilities

$$f_{AB} = c_B^{\text{ext}} = 1 - c_A^{\text{ext}} \qquad \text{and} \qquad f_{BA} = c_A^{\text{ext}} \tag{25}$$

It follows that the net flux of A into the system is (per unit volume and time)

$$J_A = (c_B^t f_{BA} - c_A^t f_{AB})/\tau = (c_B^t c_A^{\text{ext}} - c_A^t c_B^{\text{ext}})/\tau = (c_A^{\text{ext}} - c_A^t)/\tau \tag{26}$$

where τ is the unit time per step. Equation (26) accords of course with Fick's law. Take an exchange $B \to A$, giving rise to a transition from an $i(B)$ to a $j(A)$ configuration of the system. In view of Eq. (25),

$$f_{ij}/f_{ji} = c_A^{\text{ext}}/(1 - c_A^{\text{ext}}) \tag{27}$$

Furthermore, for a fluid of N ideal particles

$$p_i^t/p_j^t = (c_A{}^t)^{Nc_A^t}(c_B{}^t)^{Nc_B^t}/(c_A{}^t)^{Nc_A^t+1}(c_B{}^t)^{Nc_B^t-1} = (1 - c_A{}^t)/c_A{}^t \tag{28}$$

Using Eqs. (27) and (28), we can calculate the imbalance [Eq. (1)] associated with one $B \to A$ transition. To find the average imbalance, hence δS [Eq. (5)], this quantity has to be multiplied by the net sum of these and of the reverse transitions, viz. by J_A [Eq. (26)]. Thus (per unit volume and time)

$$\begin{aligned} \delta S/\delta t = k\tau^{-1}\overline{X^t} &= kJ_A \log(p_i^t f_{ij}/p_j^t f_{ji}) \\ &= k\tau^{-1}(c_A^{\text{ext}} - c_A{}^t) \log[c_A^{\text{ext}}(1 - c_A{}^t)/c_A{}^t(1 - c_A^{\text{ext}})] \end{aligned} \tag{29}$$

We note that $\delta S/\delta t > 0$, becoming zero when $c_A{}^t = c_A^{\text{ext}}$ at equilibrium. The second derivative is of interest:

$$\frac{\delta^2 S}{\delta t^2} = -k\tau^{-1}\frac{\delta c_A{}^t}{\delta t}\left[\log\frac{c_A^{\text{ext}}(1 - c_A{}^t)}{c_A{}^t(1 - c_A^{\text{ext}})} + \frac{c_A^{\text{ext}} - c_A{}^t}{(c_A{}^t)^2}\right] \tag{30}$$

Since $\delta c_A{}^t/\delta t = J_A$ (master equation) and in view of Eq. (26), the sign of both the logarithmic term and of $c_A^{\text{ext}} - c_A{}^t$ follows that of $\delta c_A{}^t/\delta t$. We conclude therefore

$$\delta^2 S/\delta t^2 \leqslant 0 \tag{31}$$

This result agrees with the so-called principle of minimum entropy production.$^{(11-13)}$ It is worth stressing in this context that we have considered here a *nonlinear* diffusion process. This is shown easily by defining a chemical potential of our ideal fluid,$^{(14)}$

$$\begin{aligned} (\mu_A^{\text{ext}} - \mu_A{}^0)/kT &= \log[c_A^{\text{ext}}/(1 - c_A^{\text{ext}})] \\ (\mu_A{}^t - \mu_A{}^0)/kT &= \log[c_A{}^t/(1 - c_A{}^t)] \end{aligned} \tag{32}$$

(Remark: this definition is *not* required for our calculation of δS.) Then Eq. (29) becomes

$$T\,\delta S/\delta t = -J_A(\mu_A{}^t - \mu_A^{\text{ext}}) = -J_A\,\Delta\mu_A \tag{33}$$

which resembles the generally valid expression for the dissipation function as the product of fluxes times the gradients of the conjugate thermodynamic potentials (here $\Delta\mu_A$ depends on the time). For a linear process one would require

$$(J_A)_{\text{linear}} = \text{const} \times (-\Delta\mu_A) \tag{34}$$

However, our J_A is of the form [Eq. (26)]

$$J_A = \text{const} \times (-\Delta c_A); \qquad \Delta c_A = c_A{}^t - c_A^{\text{ext}} \tag{35}$$

Equations (34) and (35) agree with one another only near equilibrium, whence $\Delta c_A \to \delta c_A$ and

$$\Delta\mu_A \to \delta\mu_A = \delta \log [c_A/(1 - c_A)] \simeq \text{const} \times \delta c_A \tag{36}$$

4. DISCUSSION

The classical calculation of entropy changes for a stochastic process is with the help of the Gibbs entropy for a total isolated system,

$$S_G = -\sum_i p_i \log(p_i/G_i) \tag{37}$$

Here the p_i are the coarse-grained probabilities of cells in the "a-space" (defining intervals of some macroscopic variable), and the G_i are the regions of the Γ-space belonging to such cells.(2) With the help of the master equation one derives(1) from Eq. (37) an expression resembling our Eq. (7),

$$\delta S_G = \tfrac{1}{2} \sum_i \sum_j (p_i f_{ij} - p_j f_{ji})[\log(p_i/p_j) - \log(G_i/G_j)] \tag{38}$$

where

$$G_i/G_j = p_i{}^\infty/p_j{}^\infty = f_{ji}/f_{ij} \tag{39}$$

The *total* system described by Eqs. (37)–(39) treats our nonisolated system simultaneously with its surroundings, as a *sub*system plus heat bath. The p_i of the total system belongs therefore to a cell defined by a given subsystem configuration (i), its value (degeneracy) being proportional to the associated number of bath configurations. Noting that constant total energy implies an effectively constant bath temperature T, we write

$$p_j{}^\infty/p_i{}^\infty = \exp(-\Delta H_{ij}/kT) \tag{40}$$

where ΔH_{ij} constitutes the enthalpy change for the transition $i \to j$. Equations (39) and (40) show the equality of the f_{ij} discussed at present to ours [Eq. (20)]. It appears therefore that the definition of δS_G in Eqs. (38)–(39) and our definition of δS [see Eq. (7)] are equivalent. However, note the following:

1. The argument just given, needed to apply Eqs. (38)–(39) to the case of a nonisolated system interacting with surroundings, seems to be rather

circumvential. Yet the nonisolated case corresponds to many actual stochastic studies of the time evolution (both theoretical(9,15–17) and by computer simulation(6–8)), as well as to the actual experimental conditions.(5)

2. In our treatment the isolation constitutes a particular case. Thus, all configurations for an isolated system at equilibrium are equally probable (microcanonical ensemble), so that [Eq. (9)]

$$f_{ij}/f_{ji} = p_j^{\infty}/p_i^{\infty} = 1 \tag{41}$$

whence [Eqs. (11)–(13)]

$$\delta S = \delta S_{\text{syst}}; \qquad \delta S_{\text{ext}} \equiv 0 \tag{42}$$

Note that $\delta S \geqslant 0$ still holds because of Eqs. (7) and (8).

3. The relevance of our detailed imbalance to irreversibility, $\delta S \geqslant 0$, seems intuitively clear: f_{ij}/f_{ji} represents the effect of the surroundings on the system, constituting a stochastic "input" or "cause"; p_i^t/p_j^t represents the ensuing change in the system's probability, constituting a stochastic "output" or "effect"; the average imbalance between the two provides a measure of irreversibility. In contrast, the relevance of coarse graining to irreversibility is less transparent. For example, a commonly expressed opinion is that S_G is inadequate since it depends on the (seemingly) arbitrary manner in which the cell volumes G_i are defined. Discussion of the stochastic process shows the opposite to be true: The definition of G_i is tantamount to that of the transition probabilities [Eq. (39)] which determine the irreversible evolution.

4. The present definition of $\delta S = \delta S_{\text{syst}} - \delta S_{\text{ext}}$ [Eqs. (11)–(13)] stresses the ease of its calculation for a model process with the help of computer simulation. Thus $-\delta S_{\text{ext}} = k\,\overline{\log(f_{ij}/f_{ji})}$ is calculated at once from the transition probabilities of an actual execution of the process. It is important to note that this calculation is valid even when the interaction with the surroundings cannot be expressed with the help of well-defined thermodynamic variables. That aspect has been described in previous articles(10) (these compute the "discrimination" of a stochastic process, which is equal to $-\delta S_{\text{ext}}$; however, the definition of δS_{syst} there is somewhat different, which makes the proof of $\delta S \geqslant 0$ difficult). The other term, $\delta S_{\text{syst}} = -k\,\delta(\overline{\log p})$, is less easy to calculate since the smallness of p_i for a many-particle system precludes direct measurement. Still, several methods enabling an indirect measurement of $\delta(\overline{\log p})$ have been described.(18–21) The model of diffusion which we have considered shows that for highly idealized systems the calculation can also be carried out analytically, without recourse to computer simulation (but very possibly such results can be always obtained from classical irreversible thermodynamics).

Summing up points 1–4, both Gibbs' and the present definition contain an extra term, in addition to $\delta S_{\text{syst}} = -k\,\delta(\overline{\log p})$, permitting one to show $\delta S \geqslant 0$. The origin of the extra term is different in the two definitions. In the former it is related to the coarse-grained cell colume (G_i), implying the need to measure p_i of a total system with reference to the *ultimate* probability distribution ($G_i \propto p_i^{\infty}$). In the latter it is due to a consideration of the *present* effect of the surroundings on a nonisolated system, $-\delta S_{\text{ext}} = \overline{\log(f_{ij}/f_{ji})}$. In a way we try to implement what Blatt(5) proposed some time ago: "Once it is admitted that the thermal motion of the wall is essential for the attainment of true equilibrium then this motion should be taken into account as such, not disguised as a coarse grained measuring process." Still, despite this difference, the two descriptions seem to be mathematically equivalent, at least insofar as f_{ij}/f_{ji} can be represented with the help of thermodynamic variables. In contradistinction, Shannon's entropy(22) (used by Jaynes,(23) for example),

$$S_s = -k \sum_i p_i \log p_i \tag{43}$$

contains no extra term and does not therefore permit one to show $\delta S \geqslant 0$. Other recent discussions of irreversible entropy(24,25) are based on Kullback's(26) definition of a probability distribution p_i relative to a *prior* distribution p_i^0. Thus

$$S_K = -k \sum_i p_i \log(p_i/p_i^0) \tag{44}$$

permitting one to show $\delta S \geqslant 0$. Despite a superficial resemblance of S_K to the Gibbs (or present) entropy, the difference lies in the interpretation of the reference probability p_i^0. The fact that p_i^0 relates to a *prior* probability makes S_K nonadditive for consecutive steps(24) and the extra term is unrelated to the transition probabilities f_{ij} (unless p_i^0 is interpreted as referring invariantly to an original equilibrium state, to which the system reverts ultimately).

Our last comment concerns the purpose which is served by the attempts to define and to calculate an irreversible entropy change, especially when not expressible by thermodynamic variables. It would be gratifying to find that the value of δS provides some absolute scale enabling one to measure the degree of irreversibility for different processes. Unfortunately, it is not clear whether and how such a measure can be employed usefully. In consolation we note other uses of studying δS: (a) Since δS_{ext} is easily calculated while δS_{syst} is not (see comment 4 above), one can vary the irreversibility of a model process in order to find the latter from the former, using $\delta S_{\text{ext}} \to \delta S_{\text{syst}}$, $\delta S \to 0$.(10) (b) A calculation showing $\delta S < 0$ indicates that a particular process describes a fluctuation away from equilibrium. Alternatively,

$\delta S' < 0$ indicates a process *driven* with the help of another, coupled process, for which $\delta S'' \geqslant -\delta S'$. (c) A theoretical expression for δS helps to identify the extensive fluxes and the conjugated intensive variables for a stochastic process, viz. generalized, possibly nonthermodynamic forces. That in turn might help the search for a minimum principle governing irreversible evolution.(11–13)

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