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Entropy of Irreversible Cooling and the "Discrimination" of Model Stochastic Processes

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Entropy changes are calculated for the irreversible cooling of a homogeneous N-particle system. The execution of an appropriate model stochastic process enables one to calculate the "discrimination" D (from the transition probabilities of the actual steps) and $\langle -D \rangle$ is shown to be equal to the external entropy change ΔS_{ext}. This is trivially true for the "Metropolis-like" processes, where the individual particles maintain a direct heat exchange with a reservoir. "Cooperative" processes, which attribute the heat exchange to the mass of N particles *in toto*, are also considered; for these ΔS_{ext} is still equal to $\langle -D \rangle$. Hence, knowing $\langle D \rangle$ and the entropy of the initial and final states of the system, one can calculate the net entropy production and study its minimization. Alternatively, a consistently probabilistic approach (independent of thermodynamic equivalents) postulates that statistical mechanical processes proceed with the least discrimination, $\mathrm{Min}\langle D \rangle$, for given conditions. The postulate is supported by its conformance with the second law of thermodynamics. $\mathrm{Min}\langle D \rangle$ reduces to the Jaynes principle both at equilibrium and for isolated systems. Computer experiments illustrating the calculation of D are presented. These describe the cooling of a square Ising lattice, with the help of the Metropolis and of the cooperative model processes; the latter, optimized for least entropy production, rapidly converge toward equilibrium.

KEY WORDS: Irreversible statistical mechanics; entropy production; information; model stochastic processes; Metropolis Monte Carlo; computer simulation; Ising lattice; cooperative relaxation.

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1. INTRODUCTION

Equilibrium statistical mechanics relates the macroscopic behavior of a many-body system to the probability distribution of its microstates, or "configurations." Specifically, if p_i are the configurational probabilities, the entropy (in k units and for countable configurations) is equal to

$$S = \mathrm{Max}\left(-\sum_i p_i \log p_i\right) = \mathrm{Max}(-\overline{\log p}) \tag{1}$$

The maximization (made intuitively plausible by Jaynes' principle of maximum uncertainty[1–3]) is with respect to the assignment of an optimal probability distribution, subject to specified constraints, such as the system's energy and volume. It fixes the proper probabilistic model, enabling the description of the system's macroscopic behavior.

Take the evolution with time of a many-body system. In analogy to systems at rest, one expects that the macroscopic behavior, and especially the entropy production due to an irreversible variation of the constraints, might be calculated with the help of a time-dependent probabilistic (stochastic) process. Since configurational probabilities p_i can be defined for any instant of a stochastic process, what suggests itself is to try and calculate the entropy changes for an irreversible process with the help of a generalization of Eq. (1),[2]

$$S^t = \mathrm{Max}\left(-\sum_i p_i^t \log p_i^t\right) = \mathrm{Max}(-\overline{\log p^t}) \tag{2}$$

However, except for the treatment of processes involving systems at steady state, or of systems slightly perturbed from the equilibrium,[2] singularly little progress has been made on the basis of such a generalized equation. This seems to be related to a certain misconception with regard to its use. Suppose a system is in an initial equilibrium state at time zero and subsequently, due to some arbitrary variation of the constraints, it is made to evolve to a new equilibrium state at t. According to Eq. (2), the entropy change associated with the evolution is

$$\Delta S = -\overline{\log p^t} + \overline{\log p^0} = \Delta S_{\mathrm{syst}} \tag{3}$$

Both quantities on the rhs of Eq. (3) constitute functions of equilibrium states, as fixed by the constraints at t and 0, respectively. Their difference cannot therefore depend on whether the constraints have been varied in a reversible or an irreversible manner! This does not imply that Eq. (3) is wrong, only that the entropy change ΔS refers to the system alone. This

[2] The definition of p_i^t is modified so as to make S^t time dependent despite Liouville's equation. See, e.g., Hobson[3] or Tolman.[4]

suffices for an isolated system but not for the description of a system which interacts with its surroundings due to the flow of heat or the action of forces. To describe the effect of the external constraints one has to take recourse to a property of a stochastic process other than $\overline{\log p}$. A brief thermodynamic preamble will help to characterize such a quantity.

For an arbitrary process involving a system and external surroundings the second law states

$$\delta\phi = \delta S_{\text{syst}} - \delta S_{\text{ext}} \geqslant 0 \tag{4}$$

Here δS_{syst} is the entropy change associated with the state of the system [as in Eq. (3)], δS_{ext} is the flow of entropy *from* the surroundings, and $\delta\phi$ is the net entropy production by the process (often called δS_{int}). If all parts of the system exchange heat with a reservoir at reciprocal temperature β_{ext}, the entry of a heat increment δQ_{syst} results in

$$\delta S_{\text{ext}} = \beta_{\text{ext}}\, \delta Q_{\text{syst}} \tag{5}$$

whence

$$\delta\phi = \delta S - \beta_{\text{ext}}\, \delta Q \geqslant 0 \tag{6}$$

Here everything except β_{ext} refers to the system and the corresponding subscript is therefore omitted. The "larger than" and the "equal to" signs refer, respectively, to an irreversible and reversible variation of the constraints. Suppose the evolution of the process is not uniquely defined by the variation of the specified constraints. Intuitively one would expect that the spontaneous tendency to self-equilibration determines a pathway which at each instant makes the entropy production as small as possible. This seems to underlie an often postulated law of irreversible thermodynamics, which says

$$\delta\phi \text{ is minimal, subject to constraints} \tag{7}$$

Consider a system undergoing an irreversible change at some stage of which two different pathways A and B present themselves, A corresponding to $\text{Min}(\delta\phi)$. Assuming that the constraints are no longer varied, and excluding fluctuations, it seems unreasonable to suppose that at a later stage B might somehow "recover lost ground," producing a value of ϕ smaller than that for A. Accepting this nonintersection of markedly different pathways, a requirement of least integral entropy production for the process is equivalent to Eq. (7) and together with Eq. (6) leads to a dictum of

$$\text{Min}\,\phi = \text{Min}\left(\Delta S - \sum \beta_{\text{ext}}\, \delta Q\right) \qquad \text{for fixed constraints} \tag{8}$$

Since ΔS is given by $-\Delta\,\overline{\log p}$ [Eq. (3)], our discussion suggests that $-\sum \beta_{\text{ext}}\, \delta Q$ constitutes the thermal analog of the required probabilistic quantity.

In the following we shall demonstrate the existence of such a quantity, called here the *discrimination* D, of a stochastic process. The discrimination D is easily evaluable (with the help of a computer) from the probabilities of the sequence of the actual stochastic transitions. Knowledge of D and of $\Delta \overline{\log p}$ (or of an equivalent change of another state function) enables us to achieve our purpose, namely to calculate the net entropy production of a particular irreversible pathway. Alternatively, a consistently probabilistic approach might be adopted to advantage: It considers D as the fundamental quantity for a stochastic description of irreversible processes, leading to probabilistic counterparts of the second law and of the principle of minimum entropy production [Eq. (8)]. Later some computer simulation results will be reported, describing "optimal" modes of cooling a square Ising lattice, so as to provide a concrete example of how the proposed theory might work in practice.

2. ΔS_{ext}, ENTROPY PRODUCTION, AND THE DISCRIMINATION OF A STOCHASTIC PROCESS

Stochastic processes will be discussed in terms of the Ising lattice cooling from an initial reciprocal temperature β^0 to β. The lattice consists of N magnetic spins, each oriented either up or down, $\sigma = \pm 1$. Near-neighbor spins i and j interact with an energy (in units J)

$$\epsilon_{ij} = -\sigma_i \sigma_j \tag{9}$$

Hence, as the lattice cools and the energy is lowered, there is a net tendency of near-neighbor spins to arrange themselves in parallel. With the help of a stochastic model, the cooling process is treated by ascribing to each spin a transition probability to flip during a unit on a time scale t, from $\sigma_i = \sigma$ to $\sigma_i = -\sigma$. As we shall see, the practical way is to treat the spin transitions one by one, which defines a parallel time scale s during a unit of which only one spin may undergo a transition. Clearly the numbers of steps on the two scales are related as

$$s = Nt \tag{10}$$

Suppose at the initial time, $t \leqslant 0$, the lattice is at equilibrium at $\beta_{\text{ext}} = \beta^0$ and at the onset of the process it is plunged into a reservoir at $\beta_{\text{ext}} = \beta$. Two possible cooling mechanisms are possible.

1. The mechanism of the cooling is such that throughout the process ($t > 0$), each spin *individually* interacts with the heat reservoir. (This can be readily visualized for a one- or two-dimensional system, or else for "hot" spins dispersed throughout a supporting medium at β_{ext}.) Consider two configurations, s and $s + 1$, adjacent on the s time scale, which differ by the

flip of a particular spin from σ to $-\sigma$. In view of Eq. (9) the energies of the two configurations differ by

$$\delta E_{s,s+1} = 2\sigma \sum_j \sigma_j \tag{11}$$

the summation extending over the interacting near neighbors of the spin. Since the exchange $\delta E_{s,s+1}$ occurs at β_{ext}, the transition probabilities, from s to $s+1$ and back, from $s+1$ to s, must obey

$$f_{s,s+1}/f_{s+1,s} = \exp(-\beta_{\text{ext}}\, \delta E_{s,s+1}) = \exp\left(-2\sigma\beta_{\text{ext}} \sum_j \sigma_j\right) \tag{12}$$

That can be established in detail by referring to the equilibrium state attained if the system were to stay in contact with β_{ext} for a long time. In that case the stationary probabilities of two adjacent configurations obey detailed balance.

$$p_s f_{s,s+1} = p_{s+1} f_{s+1,s} \tag{13}$$

while the Boltzmann distribution established at β_{ext} leads to

$$p_{s+1}/p_s = -\beta_{\text{ext}}\, \delta E_{s,s+1} \tag{14}$$

Equation (12) follows from the combination of Eqs. (13) and (14). Both the Glauber model[5] for a linear Ising lattice relaxation and the Metropolis Monte Carlo method[6],[3] are based on Eq. (12). The important feature of all such processes is that β_{ext} uniquely specifies the ratio of the forward and backward transitions at any t; nothing is therefore left for possible determination with the help of minimal entropy production.

2. The heat exchange of the individual particles at time $t > 0$ is not limited to the heat reservoir β_{ext}; it also proceeds internally through some cooperative readjustment of neighboring spins. This is the case for a three-dimensional *contiguous* mass of initially hot spins. Clearly the extent of the cooperation is related to the rates of heat transfer to β_{ext} and from spin to spin; it should disappear as the system attains equilibrium, so that β_{ext} prevails internally. For the sake of simplicity the N-spin system is treated as a homogeneous body and an appropriate *cooperative* model stochastic process describes the external and the internal heat exchange mechanisms jointly. Hence the transition probability of a spin to flip depends on the instantaneous state of its nearest neighbors [which interact with the spin in the sense of Eq. (11)] and of its more distant neighbors (which are involved in the local internal equilibration). Corresponding models are described later, in con-

[3] See Refs. 7 for application to the Ising lattice, Refs. 8 for application to the study of relaxation.

nection with the computer simulation results. Here we present a single example, illustrating our description of the cooperative cooling. The transition probability resembles the noncooperative equation (12) but depends on both near and next-nearest neighbors, j and k, respectively:

$$f_{s,s+1}/f_{s+1,s} = \exp\left[-2\sigma\left(K_1 \sum_j \sigma_j + K_2 \sum_k \sigma_k\right)\right] \tag{15}$$

K_1 and K_2 constitute adjustable parameters, and replace the definite reciprocal temperature β_{ext} of the noncooperative case. Their value, possibly time dependent, remains to be fixed with the help of the principle of minimum entropy production. For that purpose, however, the ratios of transition probabilities have to be related to thermodynamic variables.

Consider a sequence of N spin steps which varies the lattice configuration from s to $s + 1$, $s + 2$,..., until $s + N$ (when no flip occurs, adjacent configurations remain identical). The nature of the process, visiting each lattice site once and only once, allows only one connecting pathway for a particular pair of s and $s + N$ configurations. The N-step probability is therefore equal to a product of the one-step transition probabilities

$$F_{s,s+N} = f_{s,s+1} f_{s+1,s+2} \cdots f_{s+N-1,s+N} \tag{16}$$

Similarly, the product of the reverse one-step transition probabilities $f_{s+N,s+N-1} \cdots f_{s+1,s}$ is equal to the reverse N-step transition probability $F_{s+N,s}$. The increase of the *discrimination* at time t, $s/N < t \leqslant (s + N)/N$, is defined by the ratio of these two transition probabilities:

$$\delta D^t = \log(F_{s,s+N}/F_{s+N,s}) = \sum_{s'=s}^{s+N} \log(f_{s',s'+1}/f_{s'+1,s'}) \tag{17}$$

The above constitutes the outcome for a particular execution of a model stochastic process. The average value of δD^t, characterizing the model, is

$$\langle \delta D^t \rangle = \sum_\alpha p_\alpha{}^t \delta D_\alpha{}^t \tag{18}$$

where $p_\alpha{}^t$ is the probability of an α execution. For large N, however, the large number of single stochastic steps ensures that the observable outcomes do not differ markedly from the average. Thus

$$(\delta D_\alpha{}^t)_{\text{observable}} \simeq \langle \delta D^t \rangle \qquad \text{for large } N \tag{19}$$

It is now proposed that minus the external entropy change [cf. Eq. (4)] is equal to $\langle \delta D^t \rangle$ or, approximately, to $(\delta D^t)_{\text{observable}}$:

$$-\delta S^t_{\text{ext}} = \langle \delta D^t \rangle \simeq (\delta D^t)_{\text{observable}} \tag{20}$$

The proof is immediately for the noncooperative case:

$$\delta D^t = \sum_{s'=s}^{s+N} \log(f_{s',s'+1}/f_{s'+1,s'}) = -\beta_{\text{ext}} \sum_{s'=s}^{s+N} \delta E_{s',s+1}$$

$$= -\beta_{\text{ext}}\, \delta Q^t = -\delta S^t_{\text{ext}} \qquad \text{noncooperative case} \tag{21}$$

where the second equality holds identically for any execution α [see Eq. (12)], the third follows from the first law of thermodynamics, and the last holds for a system all parts of which exchange heat with a reservoir at β_{ext} [Eq. (5)].

We would like to write an analogous sequence of equalities for the cooperative case. For that purpose the bulk system, with its joint external and internal mechanisms of heat exchange, is likened to a hypothetical system all particles of which exchange heat individually at an equivalent reciprocal temperature β^t_{ext}, i.e., the cooperative cooling of a bulk system in contact with β_{ext} is equated to a noncooperative cooling at β^t_{ext}, whence β^t_{ext} is defined by the ratio of (the logarithms of) the transition probabilities and of the associated uptake of heat, in analogy to Eq. (21). [β^t_{ext} may be time dependent in view of the possible time dependence of the adjustable parameters with the help of which the cooperative transition probabilities are defined, cf. Eq. (15).] However, this ratio can be assigned the true meaning of a (reciprocal) reservoir temperature only if its value at time t is the same for any execution of the stochastic process. This cannot be strictly true, but for large enough N, β^t_{ext} should be constant to a very good approximation [cf. Eq. (19)]. Thus β^t_{ext} of the equivalent noncooperative heat exchange is formally defined and fulfills an approximate equality as follows:

$$\beta^t_{\text{ext}} = -\left\langle \sum_{s'=s}^{s+N} \log(f_{s',s'+1}/f_{s'+1,s'}) \right\rangle \Big/ \left\langle \sum_{s'=s}^{s+N} \delta E_{s',s'+1} \right\rangle$$

$$= -\langle \delta D^t \rangle / \langle \delta Q^t \rangle \simeq (\delta D^t/\delta Q^t)_{\text{observable}} \qquad \text{for large } N \tag{22}$$

so that

$$\langle \delta D^t \rangle = -\beta^t_{\text{ext}} \langle \delta Q^t \rangle = -\delta S_{\text{ext}}, \qquad \text{cooperative case} \tag{23}$$

where the second equality is due to the fact that the hypothetical noncooperative cooling at β^t_{ext} obeys Eq. (5). Equations (21) and (23) establish the validity of Eq. (20) for the noncooperative and cooperative modes of cooling. Summation of Eq. (20) for the total duration of a stochastic process, from $s = 0$ to ω, or from $t = 0$ to $\tau = \omega/N$, gives

$$(D_{0,\tau})_{\text{observable}} = \sum_{s=0}^{\omega-1} \log(f_{s,s+1}/f_{s+1,s}) \simeq \langle D_{0,\tau} \rangle = -\Delta S_{\text{ext}} \tag{24}$$

We can now return to our main purpose. Equation (4) summed and

combined with Eqs. (3) and (24) gives the probabilistic expression for the integral production of entropy

$$\phi_{0,\tau} = \langle -\log p^{\tau} \rangle + \overline{\log p^{0}} + \langle D_{0,\tau} \rangle \tag{25}$$

Here the bracketed averages are over executions (α) of a model process proceeding to τ; such averaging, of course, reproduces the barred ensemble averaging [over configurations at time τ, as in Eq. (3)]. So much for the evaluation of ϕ; the principle of minimum entropy production [Eq. (8)] then implies looking for models for which the rhs of Eq. (25) is the smallest. Two alternatives might be distinguished: First, at $t = \tau$, the system is said to have effectively attained internal equilibrium at β. If so, $\langle \log p^{\tau} \rangle$ constitutes a function of state independent of the process which took the system from $t = 0$ to τ. Then Min ϕ reduces to Min$\langle D \rangle$. Second, at $t = \tau$ the external temperature is said to have permeated the system, so that individual spins exchange heat with the reservoir at $\beta_{\text{ext}} = \beta$ (or the cooling is noncooperative for $t \geqslant \tau$). However, we do not know what the internal state of the system is at $t = \tau$, particularly whether it has or has not reached equilibrium (this indeed constitutes the generally encountered situation). A straightforward minimization of ϕ with the help of Eq. (25) is then inoperative, since one does not know how to compute $\langle \log p^{\tau} \rangle$ for the end points of arbitrary model processes. A simple subterfuge provides a way out of the difficulty. First, in view of Eq. (21), for the noncooperative cooling, we note that

$$D_{\tau,\infty} = -\beta \, \Delta E_{\tau,\infty} \tag{26}$$

or

$$D_{0,\infty} + \beta \, \Delta E_{0,\infty} = D_{0,\tau} + \beta \, \Delta E_{0,\tau} \tag{27}$$

where $t = \infty$ corresponds to the equilibrium state for β. Adding and subtracting $\beta \langle E^{\infty} \rangle$ to Eq. (25), for ϕ from $t = 0$ to ∞, therefore gives

$$\begin{aligned} \phi_{0,\infty} &= (-\beta \langle E^{\infty} \rangle + \langle -\log p^{\infty} \rangle) + \overline{\log p^{0}} + \beta E^{0} + \beta \langle \Delta E_{0,\infty} \rangle + \langle D_{0,\infty} \rangle \\ &= \log Z(\beta) - \log Z(\beta^{0}) + \beta \langle \Delta E_{0,\tau} \rangle + \langle D_{0,\tau} \rangle \end{aligned} \tag{28}$$

$Z(\beta)$, the partition function at β, is a function of state independent of the process. Minimum entropy production for the process from 0 to ∞ leads therefore to the following optimization principle for the cooling from $t = 0$ to τ:

$$\text{Min } \phi_{0,\infty} \Rightarrow \text{Min}(\beta \langle \Delta E_{0,\tau} \rangle + \langle D_{0,\tau} \rangle) \tag{29}$$

or

$$\text{Max}(-\beta \langle \Delta E_{0,\tau} \rangle - \langle D_{0,\tau} \rangle) \tag{30}$$

if the system becomes permeated by $\beta_{\text{ext}} = \beta$ at $t \geqslant \tau$. Both $\langle \Delta E_{0,\tau} \rangle$ and

$\langle D_{0,\tau} \rangle$ are evaluable for a model stochastic process with the help of computer simulation. Equation (30) therefore provides the means for the determination of an incompletely specified irreversible process.

3. A PROBABILISTIC VIEWPOINT OF THE DISCRIMINATION

We would like to take an alternative viewpoint and discuss the concept of discrimination without recourse to thermodynamic parameters. As already noted, the basic probabilistic equations (1) and (2) leads to a quantity $\overline{(\log p^t)}$ which does not allow one to distinguish between an irreversible and a reversible variation of the constraints. A quantity which could enable such a distinction to be made should possess the following properties:

1. The quantity should be expressible in terms of macroscopic variables and these should reduce to thermodynamic variables whenever an equivalent thermodynamic description exists.
2. Its evaluation should agree with the second law of thermodynamics, with the "equal to" and the "larger than" signs applying, respectively, to a reversible and irreversible variation of the constraints.
3. The description of irreversible processes with the help of the candidate quantity must be consistent with experimental evidence. It appears at the present state that such experiments can only be performed by computer simulation.

In addition, it would be desirable if the candidate quantity and the reason for its minimization could be explicable in terms of intuitive concepts. Upon consideration of Eq. (17), it can be seen that the incremental contribution to D, namely $\log(f_{s,s+1}/f_{s+1,s})$, measures the preference accorded to the transition from an old to a new configuration $(s, s+1)$ over the reverse transition $(s+1, s)$. The accumulated value of this quantity for many steps of the process therefore measures the "probabilistic effort" (or "bias," or "discrimination") with which the process achieves the change from one probability distribution to another. Thus, if the distribution does not change, $(f_{s,s+1}/f_{s+1,s})$ should be on the average equal to one; it should be greater than one if the process leads to a less random (more discriminatory) distribution. The justification for taking the logarithm of the ratio of the transition probabilities is the requirement for additivity over the individual steps of the process, which assures the extensiveness of D. Analogous to Jaynes' requirement of minimal information for the description of *systems*, we shall require least discrimination for *processes*. For an incompletely specified process one postulates accordingly

$$\text{Min}\langle D \rangle, \qquad \text{subject to constraints} \tag{31}$$

This brings us to the requirement derived before for a process proceeding from one specified state to another, namely to the first alternative considered in the discussion following Eq. (25). In the second alternative considered there, the process is such that for $t \geqslant \tau$ the system is permeated by the reservoir's $\beta_{\text{ext}} = \beta$. In that case Eq. (31) leads to

$$\text{Min}(\beta\langle E\rangle + \langle D\rangle), \qquad \text{for a system permeated by } \beta \tag{32}$$

where the derivation merely paraphrases Jaynes' argument concerning the minimization of $\overline{\log p}$ at given β (implying an effectively constant E; see Ref. 3, for example). Equation (32) is identical with Eq. (30), which has been derived with the help of a thermodynamic argument. These observations complete the intuitive description of D, of Min D, and of Eq. (32).

The fulfillment of the first of the above-listed properties has already been demonstrated in the course of our thermodynamic discussion of D [cf. Eqs. (21) and (23) for the noncooperative and cooperative cases, respectively].

The argument with regard to the second property is more complicated. Consider the contribution of step s to the discrimination [Eq. (24)], which is given by (the logarithm of) the ratio of the forward and backward transition probabilities, $f_{s,s+1}/f_{s+1,s}$. Here subscripts s and $s+1$ denote, respectively, configurations arrived at the s and $s+1$ steps of a particular process. The time-dependent probabilities of the s and $s+1$ configurations at time s (indicated in the superscript) therefore are $p_s{}^s$ and p_{s+1}^s, respectively. These probabilities are defined for any instant of time and p_{s+1}^{s+1}, for example, is the probability of the $s+1$ configuration at time $s+1$. Only pairs of configurations communicate at an s step of the process. Hence the configurational probabilities may be related to the transition probabilities by the relatively simple master equation

$$\begin{aligned} p_{s+1}^{s+1} - p_{s+1}^s = \delta p_{s+1}^{s+1} &= p_s{}^s f_{s,s+1} - p_{s+1}^s f_{s+1,s} \\ &= p_s{}^s f_{s,s+1} - p_{s+1}^{s+1} f_{s+1,s} + \delta p_{s+1}^{s+1} f_{s+1,s} \end{aligned} \tag{33}$$

which upon rearrangement becomes

$$f_{s,s+1}/f_{s+1,s} = (p_{s+1}^{s+1}/p_s{}^s)(1 + \epsilon_s\, \delta p_{s+1}^{s+1}/p_{s+1}^{s+1}), \qquad \epsilon_s = (1 - f_{s+1,s})/f_{s+1,s} > 0 \tag{34}$$

The discrimination of a particular execution [Eq. (24)] can therefore be rewritten

$$\begin{aligned} D &= \sum_{s=0}^{\omega-1} \log(f_{s,s+1}/f_{s+1,s}) \\ &= \sum_{s=0}^{\omega-1} \log(p_{s+1}^{s+1}/p_s{}^s) + \sum_{s=0}^{\omega-1} \log(1 + \epsilon_s\, \delta p_{s+1}^{s+1}/p_{s+1}^{s+1}) \end{aligned} \tag{35}$$

But

$$\sum_{s=0}^{\omega-1} \log(p_{s+1}^{s+1}/p_s^s) = \log(p_\omega{}^\omega/p_0{}^0) \tag{36}$$

Hence

$$\langle D\rangle - \langle \log(p_\omega{}^\omega/p_0{}^0)\rangle = \left\langle \sum_{s=0}^{\omega-1} \log(1 + \epsilon_s\, \delta p_{s+1}^{s+1}/p_{s+1}^{s+1}) \right\rangle \tag{37}$$

On the average δp_{s+1}^{s+1} is zero or positive. It is zero for the reversible variation of the constraints, which proceeds through a sequence of equilibrium states. Indeed, the invariance of the probabilities p_{s+1} constitutes a definition of an equilibrium state. For the nonequilibrium probability distribution corresponding to an irreversible variation of the constraints, the average δp_{s+1}^{s+1} is positive. This is because, speaking broadly, configurations that attain their maximum probability at time $s + 1$ are preferred in the averaging over configurations for the same instant of the time (subscript $s + 1$). To show this in detail [skipping the proof, one can pass to Eq. (39)], we observe that the averaging in Eq. (37) is over executions α, as in Eq. (18). To any α that reaches time $s + 1$ belongs a particular configuration for that instant, namely one with $s + 1(\alpha)$ as subscript. The probability of such an event is $p_{s+1(\alpha)}^{s+1}$. The number of different events, like the number of the Ising lattice configurations, is 2^N. Therefore the average value of $\delta p_{s+1(\alpha)}^{s+1}$ over the executions is formed by summing, for all $s + 1(\alpha)$, $\delta p_{s+1(\alpha)}^{s+1}$ multiplied by its probability $p_{s+1(\alpha)}^{s+1}$. Thus

$$\begin{aligned}\langle \delta p_{s+1}^{s+1}\rangle &= \sum_{s+1(\alpha)=1}^{2^N} p_{s+1(\alpha)}^{s+1}[p_{s+1(\alpha)}^{s+1} - p_{s+1(\alpha)}^{s}] \\ &= \sum_{s+1(\alpha)=1}^{2^N} [p_{s+1(\alpha)}^{s+1}]^2 - [p_{s+1(\alpha)}^{s+1} p_{s+1(\alpha)}^{s}] > 0\end{aligned} \tag{38}$$

In the last step of Eq. (38) the "larger than" sign is due to the fact that the (positive) autocorrelation of $p_{s+1(\alpha)}^{s+1}$ increases with decreasing displacement in time. Thus the terms $p_{s+1(\alpha)}^{s+1} \times p_{s+1(\alpha)}^{s+1}$ (with no displacement) are on the average larger than the terms $p_{s+1(\alpha)}^{s+1} \times p_{s+1(\alpha)}^{s}$ (with a displacement of one step). The positivity of $\langle \delta p_{s+1}^{s+1}\rangle$ implies in turn (by expanding the logarithm to first order) that the rhs of Eq. (37) is positive, so that

$$\langle D\rangle - \langle \log(p_\omega{}^\omega/p_0{}^0)\rangle \geqslant 0 \tag{39}$$

To complete the argument, the second term of the above equation has to be identified with ΔS. For that purpose let us recall the already mentioned very useful approximation enabling one to identify what is actually observed for large N with the average [cf. Eq. (19)]. Thus

$$(\log p_i^t)_{\text{observable}} \simeq \langle \log p^t\rangle \qquad \text{for large } N \tag{40}$$

so that

$$-\langle \log(p_\omega{}^\omega / p_0{}^0) \rangle \simeq -(\log p_\omega{}^\omega)_{\text{observable}} + (\log p_0{}^0)_{\text{observable}}$$
$$\simeq -\overline{\log p_\omega{}^\omega} + \overline{\log p_0{}^0} = \Delta S \tag{41}$$

See Eq. (3) for the last equality. Equation (39) combined with Eqs. (24) and (41) gives

$$\Delta S + \langle D \rangle = \Delta S - \Delta S_{\text{ext}} \geqslant 0 \tag{42}$$

showing that the second property, requiring agreement with the second law, is satisfactorily fulfilled.

In conclusion let it be pointed out that, whenever the variation of constraints need not be considered, our principle reduces to Jaynes' principle of minimum information. As we have just shown, for an equilibrium process $\langle -D \rangle$ becomes equal to the change of information for the system, ΔS $(= -\Delta \overline{\log p})$. For a totally isolated system $\langle D \rangle = 0$ and once again [cf. Eq. (25)] the minimization principle relates to the information alone.

4. COMPUTER SIMULATION RESULTS

Results of preliminary computer simulations of the cooling of a square Ising lattice will now be presented. The purpose of the computer experiments was twofold. First, to illustrate the application of the present theory to actual stochastic processes, notably to calculate the discrimination and the entropy production, trying to minimize its value; second, to devise modes of relaxation which might speed up the attainment of equilibrium of large cooperative systems, thereby providing an efficient alternative to the widely used Metropolis Monte Carlo method.[6–8] The second purpose thus continues previous work,[9] which dealt with the computer study of systems at equilibrium.

The following process is to be simulated: At time $t = 0$ the lattice is at equilibrium with $\beta^0 = 0$, which implies an initially random distribution. During the duration of the process the lattice is cooled to the reciprocal temperature $\beta_{\text{ext}} = \beta$ in one of three different manners, to which correspond our stochastic models I, II, and III.

Model I ("*Metropolis Cooling*"). Throughout the process the spins exchange heat individually (i.e., noncooperatively) with a reservoir at β. The transition probability for a spin to flip therefore depends on the instantaneous state of its four near neighbors, just as in Eq. (12). A "symmetrical" choice for the $\sigma \to -\sigma$ and $-\sigma \to \sigma$ transitions leads to

$$f_{\sigma,-\sigma} = 1 - f_{-\sigma,\sigma} = \exp\left(-\sigma\beta_{\text{ext}} \sum_j \sigma_j\right) \Big/ 2\cosh\left(-\sigma\beta_{\text{ext}} \sum_j \sigma_j\right) \tag{43}$$

where

$$\beta_{\text{ext}} = \beta \tag{44}$$

Such a cooling corresponds to a "T-jump" type of relaxation. Furthermore, the discrimination is identically equal to $-\beta\,\Delta E$ [cf. Eq. (12)] and there is no room for a consideration of minimum entropy production.

Model II ("*Gradual Metropolis Cooling*"). Once again the spins exchange heat individually (noncooperatively), but with a series of reservoirs which become progressively cooler with time. Thus (quite arbitrarily) the reciprocal temperature of the reservoirs β_{ext}^t is assumed to increase linearly as t increases, attaining at $t = \tau$ its ultimate value $\beta_{\text{ext}}^t = \beta$. The transition probability is therefore precisely as in Eq. (43), but with

$$\beta_{\text{ext}} = \beta_{\text{ext}}^t = \begin{cases} \beta t/\tau + a(1 - t/\tau), & t \leqslant \tau \\ \beta, & t > \tau \end{cases} \tag{45}$$

replacing Eq. (44). Here a, which corresponds to β_{ext} of the initial reservoir, constitutes an adjustable parameter. One can therefore study the dependence of the entropy production on the value of this parameter. Alternatively one can regard model II as describing the cooling of a bulk system which exchanges heat both externally with a reservoir at $\beta_{\text{ext}} \equiv \beta$ and internally through the equilibration of near-neighbor spins. [Model II then constitutes a particular case of the cooperative model III described in Eqs. (46) and (47) below, with $K_1 = \beta_{\text{ext}}^t$ and $K_2 = 0$.] In that case β_{ext}^t acquires the meaning of the reciprocal temperature which provides the *hypothetical* noncooperative equivalent of a cooperative process [see Eqs. (22)–(23)].

Model III ("*Cooperative Cooling*"). A bulk system in contact with a heat reservoir at $\beta_{\text{ext}} = \beta$ cools through a joint external and internal heat exchange. The transition probability for a spin to flip therefore depends on *two* groups of neighbors—nearest, $\sum_j \sigma_j$, and more distant, $\sum_k \sigma_k$, as already mentioned in Eq. (15). The transition probability is of the form of the Metropolis equation (43), but has two time-dependent coefficients:

$$f_{\sigma,-\sigma} = 1 - f_{-\sigma,\sigma} = \frac{\exp[-\sigma(K_1 \sum_j \sigma_j + K_2 \sum_k \sigma_k)]}{2\cosh[-\sigma(K_1 \sum_j \sigma_j + K_2 \sum_k \sigma_k)]} \tag{46}$$

where

$$K_1 = \begin{cases} \beta t/\tau + a(1 - t/\tau), & t \leqslant \tau \\ \beta, & t > \tau \end{cases} \quad \text{and} \quad K_2 = \begin{cases} b(1 - t/\tau), & t \leqslant \tau \\ 0, & t > \tau \end{cases} \tag{47}$$

The choice of this particular dependence assures that for $t \geqslant \tau$ the reservoir reciprocal temperature $\beta_{\text{ext}} = \beta$ has permeated the system internally, so that the cooperativity of individual flips disappears. Again entropy production

can be studied as a function of the two nonnegative adjustable parameters a and b which regulate the relative importance of the nearest and of the more distant interspin correlations. Two types of more distant correlations have been considered. In "model IIIa" the summation $\sum_k \sigma_k$ extends over the entire lattice, in "model IIIb" it extends over the eight second neighbors of a spin. Clearly models IIIa and IIIb represent, respectively, the extremes of the long and short range of cooperation.

The following computer results are discussed in connection with these four models. The interaction energy per spin [see Eq. (9)],

$$E = -(2N)^{-1} \sum_{i=1}^{N} \sum_{j=1}^{4} \sigma_i \sigma_j \tag{48}$$

and the spontaneous magnetization per spin

$$M = N^{-1} \sum_{i=1}^{N} \sigma_i \tag{49}$$

are both measurable for any instant of the process. Measurements of $\bar{E}$ and of $\overline{E^2}$ after equilibrium has been reached enable one to find the specific heat per spin from

$$C = \beta^2 N(\overline{E^2} - \bar{E}^2) \tag{50}$$

Finally, the measurement of the discrimination of the process [Eq. (21)] enables one to calculate the integral entropy production of the cooling, per spin, with the help of Eq. (28). Here for the initially random state, $\log Z(\beta^0) = \log 2$, while the final value $\log Z(\beta)$ is taken from Onsager's theory. Two approximations are made. Results obtained for N from 80^2 to 250^2 are compared to theoretical values of E, M, and $\log Z(\beta)$, which are for infinitely large N. Furthermore, in the spirit of Eq. (19), outcomes of particular executions of the stochastic process are identified with mean values, which also is strictly true only for infinite N.

Table I summarizes the entropy production for the cooling of a lattice with $N = 250^2$ from $\beta^0 = 0$ to $\beta = 0.5$, 0.45, 0.44, or 0.43 during $\tau = 100$ cycles per lattice. For models II, IIIa, and IIIb the results are for "optimal cooling", i.e., for values of the adjustable parameters that gave the smallest entropy production (model I has no degree of freedom left). The following gives some indication of the order of magnitude of the parameters: For model II at $\beta = 0.43$, $a = 0.08$ [Eq. (45)]; for model IIIb at the same β, $a = 0.08$ and $b = 0.7$ [Eq. (47)]. For model IIIa at $\beta = 0.5$ and 0.45, respectively, $a = 0$ and 0.02, and $b = 0.57$ and 0.28. Indeed, as might be expected, the values of a in all cases turn out to be close to zero, indicating that smallest entropy production requires that the first equivalent cooling reservoir not be markedly different from the initial state β^0. The main conclusion is that for $\beta = 0.5$, 0.45, and 0.44, the smallest entropy production,

Table I. The Entropy Production $\phi_{0,\infty}$ [Eq. (28)] for Optimized Models IIIa, IIIb, II, and I Describing the Cooling of a Lattice $N=250^2$ Starting from $\beta^0=0$ and Attaining Various Values of β

β	IIIa	IIIb	II	I	$\log Z(\beta)_{\text{theor}}$
0.5	0.0115	0.0339	0.0271	0.3356	1.0258
0.45	0.0087	0.0110	0.0130	0.2506	0.9438
0.44	0.0089	0.0098	—	0.2355	0.9287
0.43	0.0081	0.0077	0.0099	0.2221	0.9153

or optimal cooling, is obtained with the long-range cooperative model IIIa, the short-range cooperative model IIIb giving the smaller entropy production for $\beta = 0.43$. To recall, the Ising reciprocal temperature at which long-range ordering sets in is $\beta_{\text{crit}} = 0.441$, and a slightly smaller value is expected for the present lattice size.[10] The gradual Metropolis model II, which allows no correlations beyond nearest neighbors, gives a higher entropy production at all β, whereas a still larger production corresponds to the abrupt T-jump of the conventional Metropolis model I process. Furthermore, the entropy production is not very large for any of the three models, II, IIIa, and IIIb, that are allowed to cool gradually toward β during the relatively long time interval $\tau = 100$. The entropy production is, however, expected to decrease markedly as the cooling is done more gradually. This has been confirmed by optimizing the model IIIa process; for a lattice $N = 100^2$ cooling toward $\beta = 0.5$, the values of $\phi_{0,\tau}$ decrease from 0.11 to 0.05 to 0.015, respectively, as τ increases from 5 to 20 to 100.

Table II displays the values of E, M, and C for the optimal processes, i.e., those of Min ϕ in Table I. The experimental results represent time averages from $t = \tau$ to 1.2τ. Their satisfactory agreement with the theoretical values indicates that the optimal, or most reversible, modes of cooling enable the equilibrium state at β to be reached almost concurrently with the establish-

Table II. Experimental Values of the Thermodynamic Variables, at $t > \tau$, Obtained with the Models That Gave the Minimal Entropy Production in Table I, Compared with Theoretical Values for an Infinite Lattice at Equilibrium

β	Model	$-E$	$-E_{\text{theor}}$	M	M_{theor}	C	C_{theor}
0.5	IIIa	1.744	1.745	0.911	0.911	1.0	0.73
0.45	IIIa	1.507	1.513	0.745	0.749	1.8	1.61
0.44	IIIa	1.446	1.402	0.684	0	1.7	2.88
0.44	IIIb	1.352	1.402	0.11	0	3.1	2.88
0.43	IIIb	1.284	1.300	0.07	0	1.5	1.48

ment of thermal permeation, namely at times only slightly larger than τ. Once again, this seems to constitute a sensible result. Incidentally, considering the relatively large N and the proximity to β_{crit}, this agreement also indicates the potential usefulness of such most reversible modes of relaxation for the study of systems at equilibrium.

Their usefulness is further demonstrated by the results for the spontaneous magnetization as a function of time for lattices cooling toward $\beta = 0.45$ ($>\beta_{\text{crit}}$) (Fig. 1) and toward $\beta = 0.43$ ($<\beta_{\text{crit}}$) (Fig. 2). The results for $N = 250^2$ obtained with model IIIa in Fig. 1 and with model IIIb in Fig. 2 indicate that M converges quite smoothly to its theoretical value at t slightly larger than τ. In contrast, the time needed to converge to the theoretical value is much longer with the Metropolis method, and much smaller $N = 80^2$, 100^2, and 200^2 could therefore be studied. Moreover, the observed fluctuations are severe and the reproducibility for similar conditions is poor. At $\beta = 0.45$ one experiment ($N = 80^2$) converges to the theoretical value but two others, $N = 100^2$ and 200^2, do not acquire long-range order as required; the experiments at $\beta = 0.43 < \beta_{\text{crit}}$ all exhibit a meandering tendency to acquire long-range order.

As a last reasonable aspect of the results, one might mention the fact that the optimized models invariably exhibited a monotonic variation of the macroscopic variables during the cooling from $t = 0$ to τ. (A nonmonotonic variation could be obtained with a suitable choice of parameters for models IIIa and IIIb. Such processes, however, had a much larger entropy production.) An example is displayed in Fig. 3, which gives results for the afore-

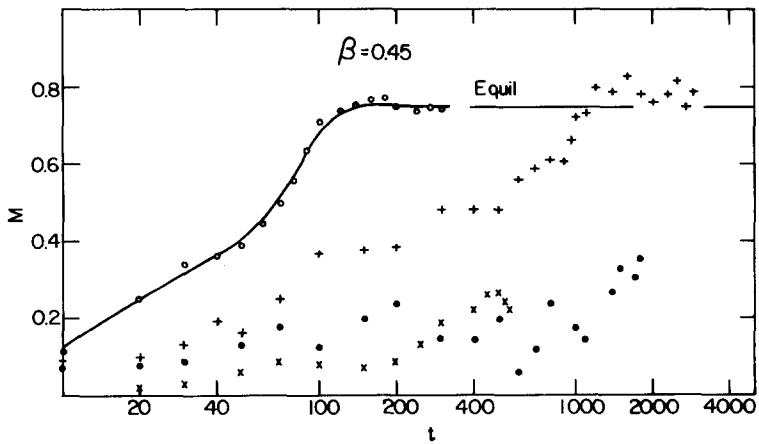

Fig. 1. The development with time t of the spontaneous magnetization M [Eq. (49)] for lattices undergoing a variation from $\beta^0 = 0$ to $\beta = 0.45$ for $\tau = 100$. The results are for: (i) the long-range cooperative model IIIa [Eq. (47)] with $N = 250^2$ (○); (ii) the Metropolis model I [Eqs. (43), (44)] with $N = 80^2$ (+), $N = 100^2$ (×), and $N = 200^2$ (●).

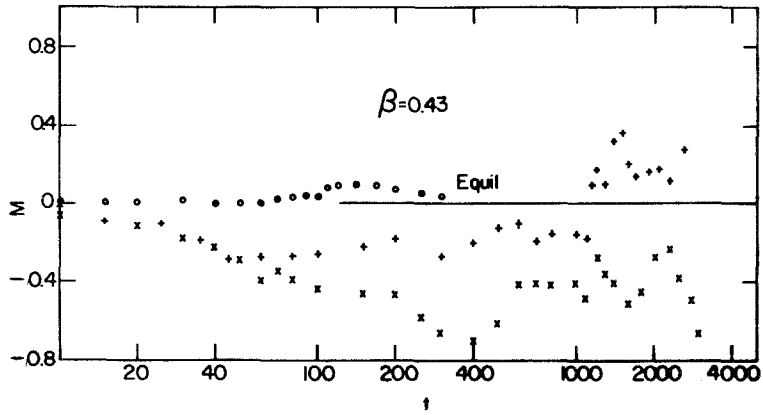

Fig. 2. Same as in Fig. 1, but for $\beta = 0.43$. The results are for: (i) the short-range cooperative model IIIb [Eq. (47)] with $N = 250^2$ (○); (ii) the Metropolis model I [Eqs. (43), (44)] for $N = 80^2$ (+, ×).

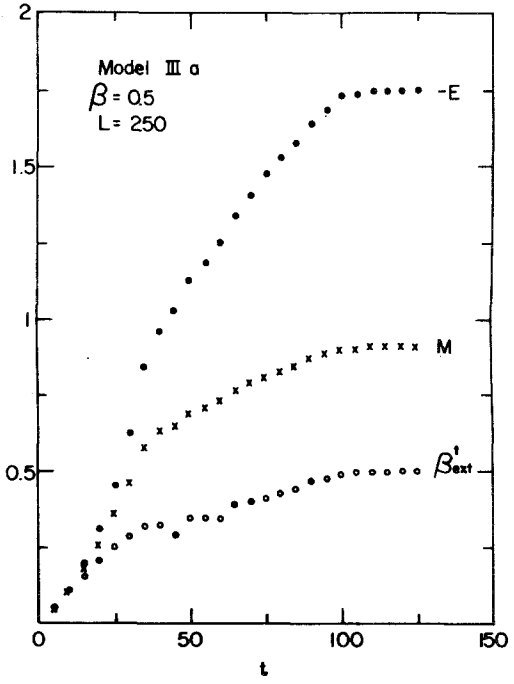

Fig. 3. The development with time t of the energy E [Eq. (48)] and spontaneous magnetization—[Eq. (49)] and of the equivalent temperature β'_{ext} [Eq. (22)] as obtained with an optimized long-range cooperative model IIIa [Eq. (47)]. The results are for a lattice of $N = 250^2$ undergoing a variation from $\beta^0 = 0$ to $\beta = 0.5$ for $\tau = 100$.

mentioned optimized model IIIa, describing a lattice $N = 250^2$ cooling toward $\beta = 0.5$ in $\tau = 100$ lattice units of time. The results are for E and M and for β^t_{ext} calculated with the help of Eq. (22), from the ratio of δD and δE.

5. CONCLUSIONS

The description of nonequilibrium behavior of macroscopic systems with the help of model stochastic processes has been considered. What is needed in this connection is a stochastic quantity with which one could evaluate the entropy change associated with the effect of constraints upon the system, ΔS_{ext}. (To recall, ΔS_{ext} and the entropy change associated with the state of the system ΔS enable one to evaluate the net entropy production ϕ and thereby to seek pathways of Min ϕ for incompletely specified processes.)

It is proposed here that the quantity to be identified with $-\Delta S_{\text{ext}}$ is the average *discrimination* of a process $\langle D \rangle$ computed from the transition probabilities of the stochastic steps [Eq. (24)]. The proposal is trivial when ΔS_{ext} for a process may be computed directly from well-defined equivalent thermodynamic variables [Eq. (21)]; it is nontrivial, however, when the definition of the thermodynamic equivalents, notably of the temperature, becomes artificial, or even doubtful. As an example, we have considered a bulk system which cools, fairly rapidly, by joint external and internal mechanisms of heat exchange, as represented by our "cooperative" model process. Another example (discussed elsewhere[11]) treats a rapid adiabatic process for which the temperature is likewise ill defined. Other examples might be provided by certain stochastic processes taken from the realms of biology, economics, or sociology (as reviewed recently[12]). In all such cases the direct evaluation of ΔS_{ext} from D would make the introduction of an ill-defined temperature quite unnecessary.

Admittedly the present proposal still requires experimental verification. Preliminary support is provided by the discussion of our computer simulation results. The proposal is also supported by its agreement with the second law of thermodynamics; this is further corroborated by D reducing to a thermodynamic expression when such is available [see Eq. (21) and, insofar as the concept of an equivalent β^t_{ext} is physically significant, Eq. (23) as well]. Finally, in the absence of varying constraints, our proposal reduces to the Jaynes' principle of minimum information, notably for a totally isolated system ($\langle D \rangle = 0$) or at equilibrium ($\langle D \rangle = \Delta \overline{\log p}$).

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