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Entropy Calculated from the Frequency of States of Individual Particles

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Entropy is related to the frequency of states for individual particles. Taking the Ising lattice as an example, a local state for an individual spin is defined by the orientation of the spin and of its neighbors. The ratio of the frequencies of two local states involved in a spin-flipping configurational transition is related to an entropy change. Implementation is by computer simulation. A stochastic process is used to construct an initial lattice configuration, corresponding to state of known entropy. This configuration is subsequently relaxed to a desired equilibrium state, with the help of a ("uniform Metropolis") Monte Carlo spin flipping and the attendant entropy change is calculated from the sequence of frequency ratios for all transitions. The calculation is approximate since it treats a process that can be described by a hypothetical sequence of states at internal equilibrium, which cannot be true for a relaxation at finite rate. Nonetheless, the results obtained have been quite accurate. The theory, therefore, provides an additional method for measuring the entropy of systems simulated with the help of a computer. It also indicates a practical way for bridging the Boltzmann entropy of individual particle states (which Jaynes has shown to be incorrect, in its original form, for strongly interacting particles), to the Gibbs entropy of N-particle configurations.

KEY WORDS: Entropy; Monte Carlo; computer simulation; Ising lattice; states of individual particles; Boltzmann entropy; Gibbs entropy.

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1. INTRODUCTION

Monte Carlo sampling of successive configurations for model N-particle systems leads to a direct measurement of average microscopic quantities, like interaction energy and enthalpy. However, entropy, hence free energy, cannot be found in that manner. Several methods have been proposed.

(a) "Thermodynamic integration." One starts from a configuration corresponding to an equilibrium state of known free energy and simulates a reversibly slow relaxation to a new equilibrium. The change in free energy is found from the reversible work, which can be computed from the simulation data. The method is time consuming because of the required slowness and runs into difficulty when phase transition is encountered on the way.[1]

(b) The method of Salsburg *et al.*[2] This computes free energy from the average reciprocal Boltzmann weight factor. The method is impractical since the main contribution to the average is from configurations of low statistical weight (large reciprocal weight factor), which for large N are impossible to sample.

(c) "Multistage sampling" of Valleau and Card.[3] One strives to find the absolute value of the configurational space belonging to given energy, hence the configurational integral and free energy. To begin with, the space belonging to the high energy levels is found in the random ensemble, the total space of which is known. The space belonging to lower energy levels is then found by proceeding to weighted ensembles (of unknown total space), in overlapping stages. The method is likewise impractical for large N, when the variation of configurational space with energy is exceedingly steep.

(d) The "stochastic models" method proposed by Alexandrowicz.[4] A typical equilibrium configuration is constructed with the help of an optimized stochastic process which allots N particles to a lattice, one after another, in succession. Entropy is computed from the (product) probability of the stepwise process. The main objection is that the method is inherently approximate.

(e) The "discrimination" method described subsequently by Alexandrowicz.[5,6] This computes the discrimination of a stochastic relaxation process from the ratio of the forward and reverse transition probabilities for the sequence of steps. In the limit of a reversible process, discrimination becomes equal to (minus) the entropy change. The method is essentially equivalent to the thermodynamic integration; its advantage lies in the direct use of stochastic quantities instead of derived thermodynamic data.

The present theory tries to relate entropy to a quantity measured microscopically for individual particles, notably to numbers giving the frequency of what we call "local states" (what are called "stochastic components" elsewhere).[7] These are best explained by an example: Each spin of a linear

Ising lattice is attributed to one of six local states, depending on its orientation and on the orientation of its two neighbors. As a system's configurations are transformed one into another with the help of a stochastic process, the frequencies of the local states vary and this variation is related to entropy changes. The variation of the frequencies is easily measured for a Monte Carlo relaxation and from this point of view the present theory constitutes an addition to the aforementioned computer methods.

Another aspect of the theory is the following. Entropy is here related to the frequency (or probability) of local states for individual particles. This resembles the Boltzmann ("H-theorem") expression for entropy, which refers to the probability of states of single particles, as opposed to the Gibbs expression, which refers to the probability of N-particle configurations in the phase space. As Jaynes[8] has very convincingly demonstrated, the Boltzmann expression is in serious error for strongly interacting particles. We shall see, however, that the present theory leads to quite accurate results for the Ising lattice which consists of strongly interacting particles. This is because our local states are not defined for an individual particle taken alone, but for a particle together with its interacting neighbors. In this sense the present theory indicates a practical way of bridging the Boltzmann and Gibbs approaches to entropy.

2. THEORY

The theory is illustrated for the square Ising lattice consisting of N spins. Spin orientations are $\sigma_i = \pm 1$ and neighbor spins i and j interact with an energy $\epsilon = -\sigma_i\sigma_j J$. Ten local states α can be distinguished according to the orientation σ_α and the energy ϵ_α of a central spin, as displayed in Table I.

Table I. The Ten Local States α for a Square Ising Lattice[a]

α	Diagram	σ_α	ϵ_α/J
1 and 2	$+\begin{smallmatrix}+\\+\end{smallmatrix}+ \rightleftharpoons +\begin{smallmatrix}+\\+\end{smallmatrix}+$	1 and −1	−4 and 4
3 and 4	$+\begin{smallmatrix}-\\+\end{smallmatrix}+ \rightleftharpoons +\begin{smallmatrix}-\\+\end{smallmatrix}+$	1 and −1	−2 and 2
5 and 6	$-\begin{smallmatrix}-\\+\end{smallmatrix}+ \rightleftharpoons -\begin{smallmatrix}-\\+\end{smallmatrix}+$	1 and −1	0 and 0
7 and 8	$-\begin{smallmatrix}-\\-\end{smallmatrix}+ \rightleftharpoons -\begin{smallmatrix}-\\-\end{smallmatrix}+$	1 and −1	2 and −2
9 and 10	$-\begin{smallmatrix}-\\-\end{smallmatrix}- \rightleftharpoons -\begin{smallmatrix}-\\-\end{smallmatrix}-$	1 and −1	4 and −4

[a] Columns 2–4, respectively, list the diagram for a pair of conjugated states, the orientation of the central spin, and the interaction energy of the central spin with its neighbors.

A set of ten numbers m_α specifies the frequency of such local states in a particular lattice configuration. Clearly,

$$\sum_{\alpha=1}^{10} m_\alpha = N \tag{1}$$

Furthermore,

$$\mu \sum_{\text{(all spins)}} \sigma_\alpha = M \tag{2}$$

and

$$\tfrac{1}{2} \sum_{\text{(all spins)}} \epsilon_\alpha = E \tag{3}$$

where M and E are, respectively, the magnetization (net orientation) and the interaction energy of a lattice configuration.

Consider the lattice to be in a hypothetical equilibrium with a (nonexistent) bath at temperature T^* in a (nonexistent) applied magnetic field H^*. Take the transition, due to the flip of the central spin, from one local state (α) to its conjugate (α'). The associated changes in the interaction energy, entropy, and magnetization of the lattice are, respectively, related by

$$\delta E_{\alpha,\alpha'} = T^* \, \delta S_{\alpha,\alpha'} + H^* \, \delta M_{\alpha,\alpha'} \tag{4}$$

The transition probabilities in the equilibrium ensemble at T^* and H^* are denoted by $F_{\alpha,\alpha'}$ and $F_{\alpha',\alpha}$. Because of the Boltzmann distribution,[5,9] we have

$$F_{\alpha,\alpha'}/F_{\alpha',\alpha} = \exp[-(E_{\alpha'} - H^*M_{\alpha'})/T^* + (E_\alpha - H^*M_\alpha)/T^*] \tag{5}$$

Or, in view of Eq. (4),

$$F_{\alpha,\alpha'}/F_{\alpha',\alpha} = \exp(-\delta S_{\alpha,\alpha'}) \tag{6}$$

Take a particular lattice configuration, with m_α spins in local state α. Any of these may give rise to an α, α' transition. The expectation value for α, α' to occur somewhere on the lattice, or the instantaneous expectation value of the α, α' "flow," is therefore proportional to $m_\alpha F_{\alpha,\alpha'}$. The expectation value of the opposite flow is proportional to $m_{\alpha'} F_{\alpha',\alpha}$. The invariance of the average values of E and of M (and of any other lattice property related to transitions among the local states) implies that on the average the two flows should be equal one to another. For large enough N, the law of large numbers (negligibly small relative fluctuations) implies that the cancellation of flows should hold for particular lattice configurations as well. Hence

$$m_\alpha F_{\alpha,\alpha'} = m_{\alpha'} F_{\alpha',\alpha}; \qquad N \to \infty \tag{7}$$

This permits transition probabilities, in the hypothetical ensemble at T^* and H^*, to be substituted by the measurable frequencies. Thus, Eqs. (6) and (7) combined lead to

$$\delta S_{\alpha,\alpha'} = \log(m_\alpha/m_{\alpha'}); \qquad N \to \infty \tag{8}$$

Suppose the lattice configurations are transformed one into another with the help of some definite stochastic process, which flips the spins—one at a time—in a sequence of steps $t' = 1, 2, 3, \ldots, t$. The sequence of steps defines a sequence of the α, α' transitions. The associated change in the entropy of our system $\Delta S_{0,t}$ then can be computed on the basis of Eq. (8), from the sequence of all frequency ratios $m_\alpha/m_{\alpha'}$ registered during the process. Noting that α and α' belong to successive instants of time, we write

$$\Delta S_{0,t} = \sum_{t'=0}^{t-1} \log[m_{\alpha(t')}/m_{\alpha'(t'+1)}]; \qquad N \to \infty \tag{9}$$

The contribution at each step is from the frequency ratio of the two states, $\alpha(t)$ and $\alpha'(t+1)$, involved in the transition. However, it will be noted that, because of the overlap of neighbor local states on the lattice, each such spin-flipping transition is accompanied by a simultaneous transformation of four more local states, not necessarily belonging to α (all these changes are quite conveniently recorded in a computer-simulated process). Furthermore, it is important to make a clear distinction between the actual stochastic process, giving rise to the α, α' transitions, on the one hand, and, on the other, the associated sequence of hypothetical transient (or "local in time") equilibria at T^* and H^*, discussed before in Eqs. (5)–(7). Transition probabilities for the latter have been denoted by $F_{\alpha,\alpha'}$. It is worth emphasizing that these hypothetical quantities do not appear in our final equation for $\Delta S_{0,t}$. Transition probabilities for the actual spin-flipping process, which incidentally need not be reversibly slow, but can correspond to a fairly abrupt relaxation (see later), are denoted by $f_{\alpha,\alpha'}$ in what follows.

Equation (9) for $\Delta S_{0,t}$ permits one to calculate the entropy of our lattice when the initial entropy is known. The procedure is as follows. An initial lattice configuration is constructed with the help of a definite stochastic process which fixes spin orientations σ_i by means of transition probabilities $p_i{}^0$ in a sequence of steps $i = 1, 2, 3, \ldots, N$. The construction determines the initial interaction energy E^0, magnetization M^0, and probability of the starting configuration

$$P^0 = \prod_{i=1}^{N} p_i{}^0 \tag{10}$$

The law of large numbers once again leads to a substantial simplification. For large enough N the (log of) the probability of a particular configuration is essentially equal to the average value associated with our initial stochastic construction

$$\log P^0 = \langle \log P^0 \rangle; \qquad N \to \infty \tag{11}$$

Statistical mechanics, however, relates entropy to $-\langle \log P \rangle$ of an assignment

of configurational probabilities (such assignment need not correspond to any equilibrium state[8]). In k units,

$$S = -\langle \log P \rangle \tag{12}$$

Equations (10)–(12) give

$$S^0 = -\sum_{i=1}^{N} \log p_i^0; \qquad N \to \infty \tag{13}$$

The initial construction is followed by the stochastic spin-flipping process of Eq. (9), giving $\Delta S_{0,t}$. Clearly $S^0 + \Delta S_{0,t}$ is the lattice entropy at time t, which need not correspond to an equilibrium state. However, to facilitate comparison to known results, we shall consider the entropy of systems at equilibrium. Suppose, therefore, that after time t the spin-flipping process converges upon a specified equilibrium state at temperature T and in the absence of a magnetic field, an example being provided by any "Metropolis" Monte Carlo relaxation.[9–11] A direct microscopic measurement and averaging of configurations for $t' \sim t$ allows us to find the equilibrium values $E(T)$ and $M(T)$. The present theory says that $S(T)$ can be estimated from a similarly direct microscopic measurement. Thus Eqs. (9) and (13) lead to

$$S(T) = S^0 + \Delta S_{0,t} = -\sum_{i=1}^{N} \log p_i^0 + \sum_{t'=0}^{t-1} \log[m_{\alpha(t')}/m_{\alpha'(t'+1)}]; \qquad N \to \infty \tag{14}$$

The two stochastic processes, the fixing of initial spin orientations and the subsequent spin flipping, have been executed with the help of a computer; actual examples are described in what follows.

3. RESULTS AND DISCUSSION

The initial stochastic construction produced lattice configurations that were partially magnetized, but with no interspin order. Thus the N-spin orientations were fixed, one after another, with the help of a constant (unconditional) transition probability

$$p^0(\sigma_i = 1) = p^0(+) = 1 - p^0(-); \qquad 1 \leqslant i \leqslant N \tag{15}$$

The following approximate equalities hold for large N [cf. Eqs. (2), (3), and (13)]:

$$M^0/N \simeq p^0(+) - p^0(-) \tag{16}$$

$$E^0/N \simeq -2[p^0(+) - p^0(-)]^2 \tag{17}$$

$$S^0/N \simeq -p^0(+) \log p^0(+) - p^0(-) \log p^0(-) \tag{18}$$

The initial construction corresponds therefore to starting from a hypothetical equilibrium at $T^* \to \infty$ and $H^*/T^* = \text{const}$. Upon its completion, the spin-flipping process convergent upon equilibrium at zero magnetic field and at a specified reciprocal "Ising temperature" J/kT was initiated. The lattice spins were flipped in an ordered succession and the N-step cycle was repeated over and over again (altogether about 300–500 cycles were performed). It is recalled that the sufficient condition for a Metropolis process to converge upon J/kT (at zero field) is for the transition probabilities of any pair of conjugated transitions to obey[5,9]

$$f_{\alpha,\alpha'}/f_{\alpha',\alpha} = \exp[-(E_{\alpha'} - E_{\alpha})/kT] \tag{19}$$

Equation (19) leaves the transition probabilities undetermined to within a multiplicative coefficient, which can make the rates different for various conjugated α, α'. Such is indeed the case with the so-called "symmetrical"[10] and "asymmetrical"[11] Metropolis methods. For the present purpose it is important that the relaxation proceeds, as far as possible, through states of local internal equilibrium. It seems preferable therefore to define a Metropolis method which corresponds to a uniform rate of energy exchange with the external reservoir, for the various conjugated α, α'. One possibility is to define a stochastic process which treats all lattice spins simultaneously, with the transition probability for each flip proportional to $\exp(-E_{\alpha'}/kT)$. Another possibility, adopted here, is to retain the convenient algorithm which treats the lattice spins one after another, but to normalize the transition probabilities of the various α, α' by a common constant, corresponding to the lowest energy level. Thus our "uniform" Metropolis method defines

$$f_{\alpha,\alpha'} = \exp[-(E_{\alpha'} - E_{\min})/kT] \tag{20}$$

where the choice

$$E_{\min} = -4J \tag{21}$$

assures that $f_{\alpha,\alpha'} \leqslant 1$ on a square lattice. The results obtained for a lattice $N = 200 \times 200$, for several values of the reciprocal equilibrium temperature J/kT and with each equilibrium attained from a few different starting configurations, are presented in Table II [much less accurate results for $S(T)$ have been obtained in trial experiments utilizing the symmetrical and asymmetrical Metropolis methods]. Columns 2–4 list the initial values of $p^0(+)$, $M^0/\mu N$, and S^0/N [see Eqs. (16) and (18)]. Columns 5 and 6 list the values of $\Delta S_{0,t}/N$ and of $S(T)/N$ as computed with the help of the present theory [Eqs. (9) and (14)]. The deviations from Onsager's theoretical values S_{th} (see, e.g., Ref. 12) are listed in the last column of the table. It is concluded that the results are quite accurate, especially when entropy increases and when the entropy contents of the initial and of the equilibrium states are not very

Table II. Computer Results of Entropy Calculations for an $N = 200 \times 200$ Lattice[a]

J/kT	$p^0(+)$	$M^0/N\mu$	S^0/N	$\Delta S_{0,t}/N$	$S(T)/N$	$[S_{th} - S(T)]/N$
0.6	0.95	0.901	0.197	−0.133	0.064	0.000^3
	0.90	0.801	0.324	−0.264	0.061	0.003^7
	0.80	0.601	0.500	−0.454	0.046	0.018^2
	0.70	0.395	0.613	−0.595	0.018	0.047^1
0.5	0.90	0.801	0.324	−0.172	0.153	0.000^5
	0.80	0.601	0.500	−0.354	0.146	0.006^9
0.4	0.80	0.601	0.500	−0.067	0.433	0.003^9
	0.50	−0.001	0.693	−0.176	0.417	0.019^5
0.3	0.95	0.901	0.197	0.382	0.579	0.000^4
	0.80	0.601	0.500	0.080	0.580	-0.000^5
	0.50	−0.001	0.693	−0.124	0.577	0.002^5

[a] Column 1 lists the reciprocal Ising temperature of the equilibrium state. Columns 2–4, respectively, give the probability of a + spin during initial construction and the resultant magnetization and entropy S^0 of the initial lattice. Columns 5–7, respectively, give the entropy change $\Delta S_{0,t}$ due to the relaxation, the entropy of the equilibrium state calculated from $S^0 + \Delta S_{0,t}$, and the deviation of the calculated value from Onsager's theory.

different. The results are less accurate for $J/kT = 0.40$, which is near the critical value $J/kT_c = 0.414$. (Attempts to study T still nearer to T_c are hampered by the extremely slow attainment of equilibrium.)

The following remarks should be added. Our method is not expected to yield the precise value of $S(T)$, since the assumption of local equilibrium at transient T^* and H^* can be strictly valid only for a reversibly slow process. This certainly is not the case with the presently described Metropolis Monte Carlo process, which corresponds to a T-jump type of relaxation. Hence the accuracy achieved is indeed pleasantly surprising! This seems to be due to the fact that short-range interspin equilibration is quite rapid, whereas the slow, long-range equilibration has a relatively small effect on first derivatives of free energy, like entropy. It is remarked further that a marked dependence of the entropy upon a spatial reorganization of an initial lattice configuration (breakdown of initial ordering of spins along lattice diagonals, for example) would render insufficient the present choice of ten local particle states, based on E_α and σ_α alone. In a way this difficulty corresponds to the well-known indeterminacy in the definition of entropy ("Gibbs' paradox"; see also Jaynes[8] on the "anthropomorphic" nature of entropy). In terms of Eqs. (4)–(5) it would require an addition of hypothetical internal work terms other than $H^* \delta M_{\alpha,\alpha'}$. The accuracy of the treatment should improve as the definition of local states is made dependent on more and more spins; in the

extreme one would pass to the (exact) Gibbs treatment of entropy in the N-particle phase space.

Despite these limitations it is concluded that the present theory provides a readily accessible and reasonably accurate method for expressing entropy by the frequency of states for individual particles. The computer execution of the method can be carried out for lattice models of any dimensionality and of any number of allowable "spin states," provided of course that interspin interactions E_α are duly specified.

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