

Concepts of nonequilibrium thermodynamics in discrete model of heat conduction

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Examples of thermodynamic evolutions toward stationary states are exhibited in a one-dimensional heat conduction problem. A computer simulation technique is employed to solve the Fourier partial differential equation and compute the evolution of the three terms in the entropy balance equation. Some concepts of linear nonequilibrium thermodynamics are analyzed in the framework of the model: the meaning of the entropy balance equation, the distinction between free and fixed forces, the role of the Onsager's relations, and the relationship between the structural adaptation of a linear system to the externally imposed constraints and the entropic concept of "order."

I. INTRODUCTION

In this paper we wish to present a discrete treatment of one-dimensional heat conduction as a vehicle for introducing the concepts of nonequilibrium thermodynamics in the linear approximation. The approach has the advantage of being transparent and easily understood. It also lends itself readily to numerical simulation methods. In Sec. II we introduce the local equilibrium hypothesis and derive the entropy balance equation. In Sec. III we present the proof of the minimum entropy production theorem, and in Sec. IV we describe the results of a computer simulation based on the model. Section V contains some observations on the relation between entropy and disorder in the context of the model.

II. ENTROPY PRODUCTION AND ENTROPY BALANCE

We consider one-dimensional heat flow in a bar with thermal conductivity k , specific heat c , and density ρ . The ends of the bar are maintained at fixed temperatures T_0 and T_n , and the sides of the bar are insulated. The length of the bar is l and its cross sectional area, assumed to be constant, is A . Once an initial temperature distribution $T_0(x)$ is prescribed, the subsequent evolution of the temperature distribution is governed by the Fourier partial differential equation

$$\rho c \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T(x,t)}{\partial x} \right). \quad (1)$$

This equation results from combining the continuity equation for the internal energy density $U(x,t)$,

$$\frac{\partial U(x,t)}{\partial t} = \rho c \frac{\partial T(x,t)}{\partial t} = - \frac{\partial}{\partial x} J(x,t), \quad (2)$$

with the Fourier assumption of a linear relation

$$J(x,t) = -k \frac{\partial T(x,t)}{\partial x} \quad (3)$$

between the heat flux density $J(x,t)$ and the temperature gradient. Owing to the externally maintained temperature gradient the system cannot relax to equilibrium. Instead it tends to a final time independent state characterized by a

nonzero transport of energy through the bar and a non-uniform temperature distribution $T_{st}(x)$. Such states are called nonequilibrium stationary states¹ or briefly stationary states. Stationary states play a role in nonequilibrium thermodynamics analogous to that played by equilibrium states in classical thermodynamics.

In nonequilibrium thermodynamics Eq. (3) is often written in the form

$$J(x,t) = LX(x,t), \quad (4)$$

where $X(x,t)$, the so-called "thermodynamic force," is the inverse temperature gradient

$$X(x,t) = \frac{\partial}{\partial x} \left(\frac{1}{T(x,t)} \right). \quad (5)$$

L and k are related by $L = kT^2$. For constant L Eq. (4) expresses the proportionality between the thermodynamic force and the corresponding flux. The assumption of constant L means of course that k is temperature dependent and conversely, a constant k would mean a temperature dependent L . Nevertheless, for sufficiently small temperature gradients, these effects will be relatively unimportant. Either Eq. (3) or (4) will be a valid approximation as long as the force (5) is not too great. This defines the range of validity of linear nonequilibrium thermodynamics.

We now wish to introduce the key concepts of entropy and entropy production, bearing in mind that entropy is defined in classical thermodynamics only for states of thermal equilibrium, whereas we are dealing here with a nonequilibrium situation. The extension of the entropy concept to nonequilibrium physics rests on the assumption of *local equilibrium*. One assumes that a nonequilibrium system may be subdivided into a large number of volume elements, such that equilibrium conditions prevail locally within each volume element. The latter must be at the same time (i) sufficiently large to allow intensive thermodynamic properties like temperature or pressure to be defined within each one, and (ii) sufficiently small so that these quantities do not vary appreciably over the size of the volume element. The assumption of local equilibrium then allows us to calculate entropy changes within each volume element by means of a Gibbs equation.

A convenient way of applying the local equilibrium hypothesis to the heat conducting bar is to set up a discrete

model. We divide the bar into $n - 1$ cells as shown in Fig. 1. Each cell j is assumed to be in a state of local equilibrium at temperature T_j . The interior cells have length $h = l/n$, while the two end sections have length $h/2$; the correctness of this subdivision procedure will be seen below. The temperatures of the end boxes are T_0 and T_n . Calling U_i the internal energy of cell i , we may then apply the local equilibrium hypothesis to write a Gibbs equation for each internal cell i :

$$dS_i = dU_i/T_i \quad (i = 1, 2, \dots, n-1), \quad (6)$$

where S and U are the entropy and internal energy of the cell. In addition we have the entropy conservation or continuity equation (2) which, in discrete form, reads

$$\frac{dU_i}{dt} = A(J_{i-1} - J_i) \quad (i = 1, 2, \dots, n-1), \quad (7)$$

where AJ_i is the rate of heat transfer from cell i to cell $i + 1$. Equation (7) states that the rate of heat accumulation in cell i is equal to the algebraic sum of the heat transfer rates to the cell. Note that AJ_0 is the rate of heat transfer to the bar from left-hand reservoir and that similarly AJ_{n-1} is the heat transfer rate from the bar to the right-hand reservoir. Summing Eq. (6) over i and using Eq. (7) yields

$$\frac{dS}{dt} = A \sum_{i=1}^{n-1} \frac{1}{T_i} (J_{i-1} - J_i) \quad (8)$$

for the time derivative of the total entropy of the bar. By adding and subtracting $AJ_0/T_0 + AJ_{n-1}/T_n$ to the right-hand side and rearranging terms, Eq. (8) becomes

$$\frac{dS}{dt} = \frac{AJ_0}{T_0} - \frac{AJ_{n-1}}{T_n} + \sum_{i=0}^{n-1} AJ_i \left(\frac{1}{T_{i+1}} - \frac{1}{T_i} \right). \quad (9)$$

Equation (9) is known as the entropy balance equation. It exhibits the entropy variation as the sum of two terms

$$\frac{dS}{dt} = \frac{d_i S}{dt} + \frac{d_e S}{dt}, \quad (10)$$

where $d_i S/dt$ and $d_e S/dt$ are, respectively, the internal entropy production and the external entropy transfer:

$$\frac{d_i S}{dt} = \sum_{i=0}^{n-1} AJ_i \left(\frac{1}{T_{i+1}} - \frac{1}{T_i} \right), \quad (11a)$$

$$\frac{d_e S}{dt} = \frac{AJ_0}{T_0} - \frac{AJ_{n-1}}{T_n}. \quad (11b)$$

The entropy production $d_i S/dt$ is of particular importance in nonequilibrium thermodynamics. The second law requires that this quantity be non-negative, i.e., $d_i S/dt \geq 0$, where equality holds for reversible processes only. Thus the entropy production is positive for any system undergoing irreversible processes. We note from Eq. (11a) that the entropy production has the form of a sum of products of thermodynamic forces and fluxes, i.e.,

$$\frac{d_i S}{dt} = \sum_{i=0}^{n-1} AJ_i X_i \quad (12)$$

with

$$X_i = T_{i+1}^{-1} - T_i^{-1}. \quad (13)$$

Also observe that in the particular case of two reservoirs at the same temperature, i.e., $T_0 = T_n = T$, the entropy balance equation reduces to

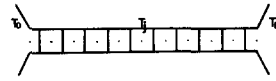


Fig. 1. Discrete model of a heat conducting bar.

$$\begin{aligned} \frac{d_i S}{dt} &= \frac{dS}{dt} - \frac{d_e S}{dt} = \frac{dS}{dt} - \frac{1}{T} A(J_0 - J_n) \\ &= \frac{d}{dt} \left(S - \frac{1}{T} U \right), \end{aligned} \quad (14)$$

where we have used Eq. (7) with $U = \sum_{i=1}^{n-1} U_i$. Thus the entropy production in this case is proportional to the time derivative of the thermodynamic potential $S - U/T$, where T is the reservoir temperature. As a general rule, the entropy production can be expressed as the time derivative of a thermodynamic potential if and only if the external constraints are such that the system is allowed to relax to equilibrium. In the case of nonequilibrium constraints, the stationary state is characterized by a constant nonzero value of the entropy production. A more precise characterization of the stationary state will be given in the following section.

A further point concerns the method of subdivision into cells introduced earlier. Equation (11a) is the discrete transcription of the continuum expression

$$\frac{d_i S}{dt} = \int d^3x AJ(x) \frac{\partial}{\partial x} \left(\frac{1}{T(x)} \right),$$

and we note that it appears correctly as the sum of n terms and not $n - 1$ terms as would have been the case had we subdivided the bar into n equal cells. Our method of subdivision ensures that there are exactly n points coinciding with the internal cell boundaries at which irreversible transfers of heat can take place and each cell boundary contributes one term to the entropy production. The reader may wish to compare the derivation of the entropy balance equation given above with the corresponding derivation in the continuum case as given for example in Refs. 2 or 3. One advantage of the discrete approach adopted here is that it makes the origin of the entropy production term completely transparent. One thereby avoids the conceptual difficulties which arise in attempting to visualize the entropy flow "in terms of an anomalous fluid capable of being destroyed and created."²

A further important advantage of the discrete approach is that it readily lends itself to numerical computation. In Sec. IV we describe a computer simulation to calculate the time dependence of the three terms in the entropy balance equation. The necessary formulas are based on Eqs. (11a) and (11b), together with Fourier's law (3) in its discrete form,

$$J_i = (-k/h)(T_{i+1} - T_i) \quad i = 0, 1, \dots, n-1. \quad (15)$$

This yields

$$\frac{d_i S}{dt} = -\frac{Ak}{h} \sum_{i=0}^{n-1} (T_{i+1} - T_i) \left(\frac{1}{T_{i+1}} - \frac{1}{T_i} \right), \quad (16a)$$

$$\frac{d_e S}{dt} = -\frac{Ak}{h} \frac{1}{T_0} (T_1 - T_0) + \frac{Ak}{h} \frac{1}{T_n} (T_n - T_{n-1}). \quad (16b)$$

Using Eqs. (16a) and (16b), $d_e S/dt$, $d_i S/dt$, and dS/dt may be computed in terms of the T_i for any time t . For a com-

puter simulation we also require the evolution equations for the $T_i(t)$. These are obtained by setting

$$\frac{1}{Ah} \frac{dU_i}{dt} = \rho c_v \frac{dT_i}{dt}, \quad (17)$$

where ρ is the density, c_v is the constant volume specific heat, and Eq. (7) is used together with Eq. (15). This yields the set of ordinary differential equations

$$\frac{dT_i}{dt} = \frac{\alpha}{h^2} [(T_{i+1} - T_i) - (T_i - T_{i-1})], \quad (18)$$

where $\alpha = k/\rho c_v$ is the diffusivity. Equation (18) is, of course, just the discrete transcription of Fourier's Eq. (1).

III. THEOREM OF MINIMUM ENTROPY PRODUCTION

The linear domain of nonequilibrium thermodynamics is characterized by an extremum principle known as the theorem of minimum entropy production. First established by Prigogine in 1947, this principle⁴ states that in the stationary state the entropy production takes on the minimum value compatible with the external constraints. In the particular case when the external constraints are such that the system may relax to equilibrium the entropy production takes on its minimum value of zero.

The theorem of minimum entropy production is based on a mathematical characterization of nonequilibrium stationary state. How are such states to be defined? The requirement that $dS/dt = 0$ or equivalently that

$$\frac{d_i S}{dt} = -\frac{d_e S}{dt}$$

is a necessary condition for a stationary state, but is not sufficient. The correct definition of stationary state hinges on the distinction between *fixed* forces and *free* forces. In the example of the heat-conducting bar this distinction emerges clearly when we transform to a different representation of the thermodynamic fluxes and forces. We define new forces F_i by

$$\begin{aligned} F_0 &= X_{n-1} + \dots + X_0 = T_n^{-1} - T_0^{-1}, \\ F_1 &= X_{n-1} + \dots + X_1 = T_n^{-1} - T_1^{-1}, \\ &\vdots \\ F_{n-1} &= X_{n-1} = T_n^{-1} - T_{n-1}^{-1}, \end{aligned} \quad (19)$$

and conjugate fluxes I_i such that

$$\frac{d_i S}{dt} = \sum_{i=0}^{n-1} A J_i X_i = \sum_{i=0}^{n-1} A I_i F_i. \quad (20)$$

A short calculation then shows that the I_i must be related to the J_i by

$$\begin{aligned} I_0 &= J_0 \\ I_1 &= J_1 - J_0 \\ I_2 &= J_2 - J_1 \\ &\vdots \\ I_{n-1} &= J_{n-1} - J_{n-2}. \end{aligned} \quad (21)$$

The new representation of forces and fluxes has the merit of explicitly separating out the one fixed force $F_0 = T_n^{-1} - T_0^{-1}$ from the remaining $n-1$ variable or free forces F_k

($k = 1, \dots, n-1$). The stationary state is now completely characterized by the requirement that the fluxes conjugate to the free forces shall vanish:

$$I_1 = I_2 = \dots = I_{n-1} = 0. \quad (22)$$

In terms of the J_i , this is simply the requirement that $J_0 = J_1 = \dots = J_{n-1}$ by virtue of (21).

In the old representation the proportionality of fluxes and forces, Eq. (4), took the form

$$J_i = L X_i, \quad i = 0, 1, \dots, n-1. \quad (23)$$

In the new representation, Eq. (23) yields the more general linear relations

$$\begin{aligned} I_0 &= L F_0 - L F_1, \\ I_1 &= -L F_0 + 2L F_1 - L F_2, \\ &\vdots \\ I_k &= -L F_{k-1} + 2L F_k - L F_{k+1}, \\ &\vdots \\ I_{n-1} &= -L F_{n-2} + 2L F_{n-1}. \end{aligned} \quad (24)$$

These relations are of the form

$$I_i = \sum_j L_{ij} F_j, \quad (25)$$

with the matrix L_{ij} satisfying the important Onsager relations⁵:

$$L_{ij} = L_{ji}. \quad (26)$$

To prove the minimum entropy production theorem we now use Eq. (25) to write

$$\frac{d_i S}{dt} = A \sum_{i=0}^{n-1} I_i F_i = A \sum_{i,j} L_{ij} F_i F_j \quad (27)$$

and take the derivatives of (27) with respect to the free forces F_k ($k = 1, \dots, n-1$) leaving F_0 constant,

$$\begin{aligned} \frac{\partial}{\partial F_k} \left(\frac{d_i S}{dt} \right) &= A \sum_j (L_{kj} + L_{jk}) F_j = 2A \sum_j L_{kj} F_j \\ &= 2A I_k \quad k = 1, 2, \dots, n-1. \end{aligned} \quad (28)$$

Hence the conditions (22) defining the stationary state are equivalent to the extremum conditions

$$\frac{\partial}{\partial F_k} \left(\frac{d_i S}{dt} \right) = 0 \quad (29)$$

and since dS/dt is a positive definite quadratic form, the extremum defined by (29) must be a minimum. It is important to note the crucial role played by both the linear relations (25) and the Onsager symmetry relations (26) in the above proof.

IV. COMPUTER SIMULATION

In this section we describe the results of a computer simulation based on the discrete model of Sec. II for a bar of constant cross section $A = 1 \text{ cm}^2$ and length $l = 10 \text{ cm}$. For a hypothetical metal we take the conductivity, density and specific heat to be $k = 1.0 \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ K}^{-1}$, $\rho = 10.5 \text{ g cm}^{-3}$, and $c = 0.05 \text{ cal g}^{-1} \text{ K}^{-1}$. These are in fact realistic values for a metal in the 200–400 K temperature range. The goal of the simulation experiment is the computation of the three terms in the entropy balance equation during the evolution of the temperature distribution from various given initial configurations to the final configuration, the latter

being determined by the fixed temperature constraints on the two external reservoirs. The evolution of the temperature distribution as a function of time is computed from Eq. (18). For each instantaneous temperature distribution, the value of $d_e S/dt$, $d_i S/dt$, and dS/dt are computed by means of Eqs. (16a), (16b), and (10).

For the division of the bar into cells we set $n = 10$ corresponding to a total of 11 cells in Fig. 1: two end cells of length 0.5 cm and nine inner cells of length 1 cm. For the reservoir temperature we set $T_0 = 360$ K and $T_n = 240$ K. These temperatures are maintained fixed throughout, while the temperatures of the inner cells are recomputed every tenth of a second by straightforward finite difference integration of Eq. (18), given an initial temperature distribution T_1, T_2, \dots, T_9 at $t = 0$. Results for three different initial temperature distributions are displayed in Fig. 2, which also exhibits the time evolution of the temperature distributions taken every 2 sec. In each case the computations were cut off at $t = 20$ sec. As can be seen from the results, this provided ample time for the temperature distribution to reach its stationary value to within less than 0.1%.

It might seem at first sight that setting $n = 10$ would not provide a sufficiently fine grid for reasonable accuracy of the simulation technique. A further question is the error introduced by our choice of 0.1-sec time intervals. We have therefore checked the overall accuracy by applying it to a similar diffusion problem for which a Fourier solution has been computed by Abraham.⁶ Comparison of the temperature distributions computed by the present method with Abraham's results shows a deviation of less than 1% over the entire time slice considered by Abraham.⁷ This is of the same order as the experimental error in k and it is therefore

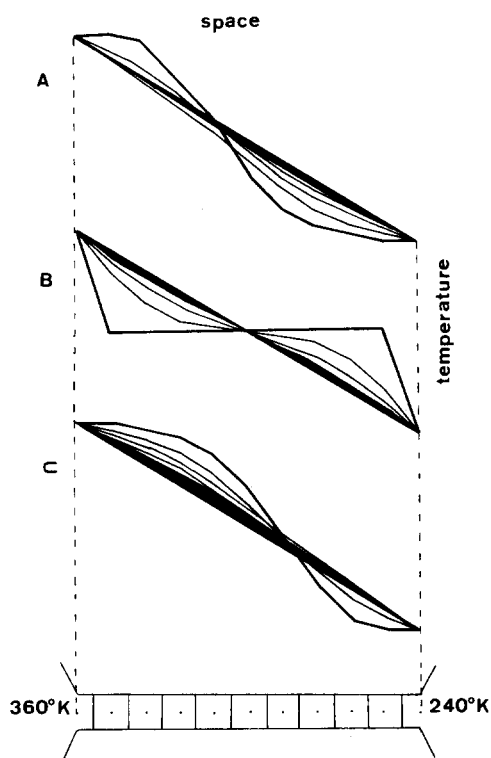


Fig. 2. Time evolution of temperature configurations at 2-sec time intervals for the three different cases. In each case computations were cut off at $t = 20$ sec.

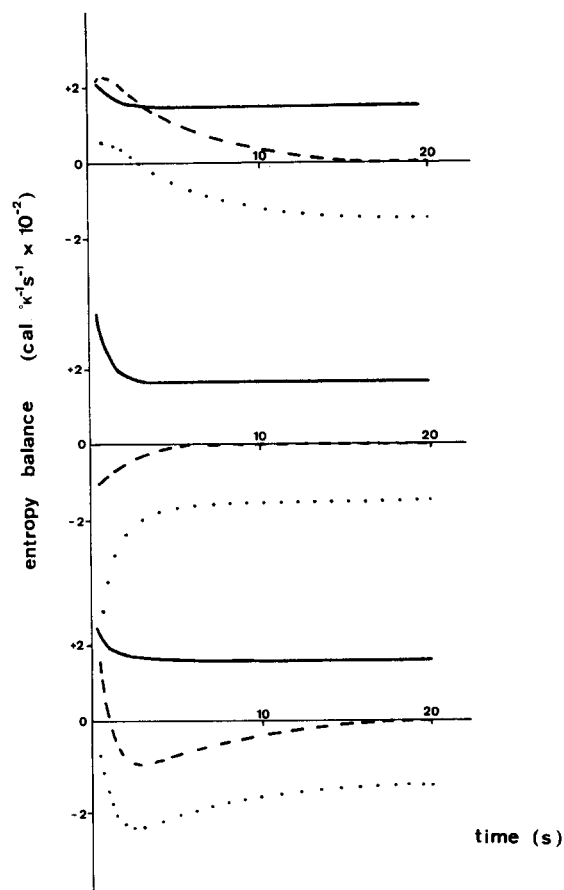


Fig. 3. Time evolution of the three terms in the entropy balance. Solid lines denote $d_i S/dt$, dotted lines denote $d_e S/dt$, and dashed lines denote dS/dt .

clear that little would be gained by further refinement of the space and time grids.

We now turn to the computation of $d_i S/dt$, $d_e S/dt$, and dS/dt . Application of Eqs. (16a), (16b), and (10) at each time point of the simulation yields the curves plotted in Fig. 3 for each of the three initial temperature distributions. In particular, the question as to whether S increases or decreases turns out to be crucially dependent on the values of the initial temperatures. The entropy change can of course be computed by numerical integration of the dS/dt curves shown in Fig. 3, but a simpler procedure is to use the formula

$$\Delta S = \sum_{k=1}^9 \Delta S_k = \rho c \sum_{k=1}^9 \ln \frac{T_k^{\text{stat}}}{T_k^{\text{init}}}, \quad (30)$$

which follows from the local equilibrium assumption for each cell by setting $dS_k = dQ_k/T_k = \rho c dT_k/T_k$, integrating over T_k and summing on k .

Also noteworthy is the form of the $d_i S/dt$ curves displayed in Fig. 3. In each case the entropy production decreases monotonically in accordance with the minimum entropy production theorem. Some slight deviation from this behavior can be observed, as in case A for example. These deviations arise because the theorem is in fact strictly applicable only when the relation between fluxes and forces is taken to be $J = L \nabla(1/T)$ with constant L . Here the simulation has been based on Fourier's law $J = k \nabla T$ [see Eq. (15)] with constant k to take account of the experi-

mentally observed constancy of the thermal conductivity in the temperature range we have considered.

V. ORDER

The results of Sec. IV allow some interesting observations to be made as to the meaning of the term "order" in the context of a thermodynamic evolution of the type considered in this paper. A frequently discussed⁸ aspect of this evolution is the fact that while the entropy production must always be positive as a result of the second law, the entropy variation dS/dt can be either positive or negative. If in the entropy balance equation $dS = d_i S + d_e S$, the entropy transfer term $d_e S$ is negative and greater in absolute value than the entropy production term $d_i S$, the entropy of the open system will decrease, thereby allowing the system to evolve toward a state of greater "order." The most commonly cited example of this phenomenon is the Knudsen effect in which two vessels I and II connected by a narrow orifice are filled with gas and a temperature difference is maintained between the vessels. Starting from an initial state in which the gas is evenly distributed between the two vessels, the gas will tend to flow from the hot vessel to the cold vessel. As the system evolves toward its stationary state of minimum entropy production, a pressure differential is built up and attains the value

$$p^I/p^{II} = (T^I/T^{II})^{1/2} \quad (31)$$

in the stationary state. The difference between the entropies of the initial and final states can be calculated and the entropy of the gas decreases during the evolution. To sum up, an originally homogeneous distribution becomes inhomogeneous and the decrease in S is thereby associated with an increase in the order of the system.

Consideration of the simpler case of heat conduction shows, however, that while the creation of a gradient may intuitively appear to correspond to an increase in order, it need not correspond to an entropy decrease. It may in fact reflect an increase in entropy. To see this, assume the initial temperature configuration to be $T_i = 240$ K for all $i = 1, 2, \dots, n-1$ and allow it to evolve with the same nonequilibrium constraints as in Sec. III. As is clear from Eq. (30), the initially homogeneous temperature distribution has a lower entropy than the final stationary distribution even though the latter exhibits a gradient. Conversely a decrease in en-

tropy can correspond to a homogenization process if instead of considering the temperature T_i we focus attention on the flux currents J_i ($i = 0, 1, \dots, n-1$). Independently of whether ΔS is positive or negative, the currents J_i will tend to equalize during the evolution, as is clear from the theorem of minimum entropy production. Here the destruction of a gradient may accompany a decrease in S . The relationship between entropy and "order" taken in the sense of inhomogeneity is seen to be far from clear cut.

Extending this line of reasoning, it would appear that the only one-to-one connection that can be drawn between entropy and order in simple models of the type analyzed here is the connection which follows from Boltzmann's equation relating S to the number of available microstates W . For each internal cell ($i = 1, 2, \dots, n-1$) the assumption of local equilibrium allows us to set

$$\Delta S_i = S_i^{\text{stat}} - S_i^{\text{init}} = k \ln W_i^{\text{stat}}/W_i^{\text{init}}, \quad (32)$$

which yields the relation

$$\Delta S = k \sum_{i=1}^{n-1} \ln \frac{W_i^{\text{stat}}}{W_i^{\text{init}}} = k \ln \frac{W^{\text{stat}}}{W^{\text{init}}} \quad (33)$$

between the total entropy change of the bar and the total number of available microstates $W = \prod_{i=1}^{n-1} W_i$ corresponding to initial and final states. A decrease in S signifies a decrease in W , which can in turn be interpreted as an increase in "order." This notion of order is however quite specific and has little direct connection with the existence or nonexistence of macroscopic gradients.

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⁶F. F. Abraham, *Introduction to Computer Simulation in Applied Science* (Plenum, New York, 1972).

⁷Abraham's Fourier solution is accurate to within 5 parts in 1000 in this interval.

⁸See, for example, Ref. 2 or E. Schrödinger, *What is Life?* (Cambridge University, New York, 1944).