Inadequacy of entropy and entropy derivatives in characterizing the steady state

Rolf Landauer
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
(Received 30 October 1974; revised manuscript received 13 January 1975)

In bistable systems the transition kinetics between the two locally stable states can be altered without changing the behavior in the immediate vicinity of the two favored steady states. It follows that quantities which characterize only the vicinity of the favored states cannot determine the most probable state. A second point: Even in monostable linear circuits the steady state need not correspond to minimum entropy production.

There has been a growing interest in the nonequilibrium steady state. Entropy, entropy generation, and the nonlinear variation of the entropy about the state in question have been treated in a diverse stream of papers, far too numerous for citation but with several central thrusts. The work by Jaynes,[1] as elaborated by Zubarev and Kalaschnikov,[2] by Corbet and Morowitz,[3] and others, assigns entropy the same role as in equilibrium statistical mechanics. In this approach, entropy represents a lack of information, and is maximized subject to constraints imposed on the system. A second line of attack is based on the work of Glansdorff and Prigogine[4] and a related but independent approach by Schlögl.[5] These theories take the nonlinear changes of the entropy about a steady state, or else the "excess entropy production," and utilize these quantities in stability criteria. Finally there is the older work by Prigogine[6] which stresses that entropy generation is at a minimum in the steady state for systems "sufficiently close to equilibrium."

Work of this sort seems motivated by the attempt to find a quantity which plays the same pivotal role in the steady state as energy does in equilibrium. In equilibrium, the state with the lowest energy is the most probable state, and more generally, $e^{-\beta H}$ describes the relative probability of occupation of higher-energy states. We can write down this probability without any need to follow the system through its detailed motion. If there is more than one locally stable state, $e^{-\beta H}$ still gives us the relative occupation probabilities at the several points of local stability, without any need to invoke the behavior at the intervening potential barriers.

This paper points out that in general, in the steady state, we cannot expect to find any simple expressions of this sort. We shall show that there can be no quantity which depends only on the immediate neighborhood of interest and which determines the relative probability of occupation of that neighborhood. Thus entropy, entropy time derivatives, or nonlinear entropy variations are inadequate to specify the probability of occupation of one stable or metastable state relative to another such state. In a separate comment, at the end of this paper, we also show that the principle of minimum entropy generation is limited to the role of a frequently useful approximation, rather than being a basic physical principle. It has, of course, always been clear that in systems which depart from equilibrium behavior in a very microscopic way, e.g., turbulence or non-Maxwellian hot-electron distributions, we need a detailed concern with the kinetics of the system's behavior. This paper, however, is limited to simpler systems in which only a few macrovariables are required to be far from equilibrium.

In the case of some steady-state systems, which permit more than one locally stable state, we have learned how to compute the relative probability of occupation of such states.[7-9] We can use these known results to judge the limitations of the entropy-oriented approaches, and in a separate publication[10] the author will invoke tunnel diode circuits as a vehicle for that analysis. Here, we shall use another model, chosen because it can be understood without detailed dependence on the existing literature.[7-9]

Our basic point: We can modify a system, such as a particle in the potential shown in Fig. 1(a), in such a way that the system behavior and all the

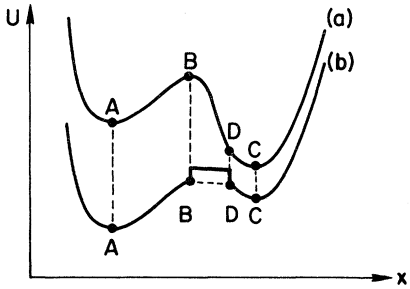

FIG. 1. (a) Bistable potential well with A metastable relative to C. (b) D has been raised to level of B to illustrate effect of heating BD.

local properties near state A and C remain unaffected; but by going away from equilibrium we can change the kinetics over a range of the intervening states. Thus we can change $\rho(C)/\rho(A)$, where ρ is the distribution function, without changing the entropy associated with either C or A, and without changing any of the time or x derivatives of entropy, near A or C. It is therefore impossible to use a purely local characterization to predict the system's preferred state. The detailed kinetics along the path connecting C and A must be involved.

Consider motion in a heavily overdamped potential, as shown in Fig. 1(a). The probability distribution ρ for a particle in this potential is given by $e^{-U/kT}$, and this favors the neighborhood of C relative to that of A. For subsequent use, note that curve a can be taken as a plot of $-kT\log\rho$. Now let us modify the temperature along a range of the x coordinate, say between B and D. If we bring BD to a very high temperature, then $e^{-U/kT}$ will be a very flat distribution, and ρ will be independent of U and x in that range. Elsewhere we have kept the original temperature, and therefore the same relative variation of the distribution function. Thus, the shape of $-\log\rho \sim U/kT$ has been left unchanged to the left of B, similarly to the right of D. We have, however, as a result of the high temperature in the range BD made $\log\rho$ independent of x. Thus the new curve of $-\log\rho$ is given by curve b which is identical in shape to a, except for the leveling shown by the dashed line between B and D. (The significance of the solid line, showing a rise between B and D, will be discussed later.)

Thus by modifying the behavior in the range BD, we have changed the relative probability of occupation of A and C and have changed C to the less likely state. In Fig. 1(a) as sketched, ρ is greater at D than at A, but this is not essential for the argument. The range BD can be chosen to lie entirely above the energies of both A and C, and if the energy at the unstable point B is high enough, the same conclusion can still be reached: C can become the less likely state.

We have thus modified the relative probabilities of A and C, without modifying the behavior near A or C, but only in the sparsely occupied states in between. Thus any local quantity characterizing the behavior near A or C will have been left unchanged and cannot serve as an indicator of the favored state or of the stability of a distribution.

The argument just given requires subsidiary remarks about the role of the points B and D at which the temperature discontinuities occur. First of all, the temperature of our particle cannot be strictly discontinuous as a function of x. After crossing either B or D, the particle must take a little while to come into equilibrium with its new temperature. The greater the damping, however, the more rapid the adjustment will be. Thus the range of x over which deviations from the correct "local" Boltzmann distribution occur can be minimized to any desired degree. Within this range of deviation, the steady-state distribution ρ is affected not only by the potential but also by gradients in particle temperature. Assume, as indicated, that the temperature variation occurs over a range of x small enough so that the potential gradient has no appreciable effect on ρ within this range. In this range we are therefore concerned primarily with the effects of the temperature variation. At D, for example, particles from the right arrive with a lower velocity than particles from the left. To achieve the zero-current flow required in the steady state, the density must, therefore, drop as we go into the high-temperature range. This is shown by the solid portion of Fig. 1(b) between B and D. The situation at B, however, is entirely analogous to the one at D with the same temperature changes, and therefore, the same drop in ρ upon moving from the cold range into the hot range. Thus the net effect of the more accurate solid portion BD of Fig. 1(b) is the same as that of the original dashed line, and the hot zone still provides the indicated leveling action.

Have we not also changed entropy generation by introducing the heating apparatus for the range BD? To answer this, note first that the actual well structure, aside from the particle motion, need not be thermally conducting. In particular, the "material" between BD could be thermally disjoint from the remaining portions of the well, so that only the particle motion itself acts as a source of heat transport between BD and the surrounding colder portions. If BD, however, is in a low-probability range, such particle crossings will be rare, and the associated entropy production can be very small and by suitable well choice, made arbitrarily small. In any case entropy generation associated with passage through D, for example, is not part of the immediate neighborhood characterization of C, if C and D are far enough apart in energy. Any other entropy production associated with the heating of BD is equally present, whether the particle is near A or near C, and does not enter into a comparison of quantities between A and C.

Our conclusion can be illustrated via an example suggested by C. H. Bennett. To determine whether under a given set of planetary conditions life is the preferred state or only a metastable state, we cannot just compare the lifeless state and the known biological state, but must consider the

transitions between these states. Furthermore, we must go beyond ensemble averages and must take fluctuations (analogous to the temperatures in Fig. 1) along the transition paths into account.

We now break from the preceding for a comment applicable to monostable systems. The steady state is frequently characterized as a state of minimum entropy production. This principle can only be expected to apply for steady states which are not too far from equilibrium.[6] The intuitive appeal of the principle is exemplified by a typical quotation[11]: "Since it is to be expected that the steady state will be as near the equilibrium state as the various constants will allow, we expect the entropy production rate to be as small as possible."

Recent extensions[12] of $dQ = T\,dS$ to steady-state systems far from equilibrium have required evaluation of the energy dissipation in a slowly modulated system whose entropy is changing. Let λ be some modulation parameter, e.g., the battery voltage in a circuit. Compare the dissipation in a circuit slowly being taken through $\lambda = \lambda_0$ with the dissipation in a circuit which has reached the steady state for $\lambda = \lambda_0$. Minimal entropy production would suggest that the modulated circuit has a higher dissipation, and that this difference is second order in $d\lambda/dt$. In actual fact,[12] the difference is generally first order and reversible; i.e., it changes sign together with $d\lambda/dt$. Even in the case of strictly linear circuits, where we might expect the validity of the minimal entropy production theorem to be unlimited by the restriction to systems "not too far from equilibrium," we find that minimal entropy production does not apply. Consider, for example, a voltage source across a resistance in series with an inductance. Now increase the battery voltage slightly. As we approach the new steady state, during a period determined by the L/R time constant of the circuit, *the resistive current and therefore the dissipation increase steadily*. They do so for all initial values of battery voltage, i.e., for conditions arbitrarily close to equilibrium. Without specifying the exact domain of validity of minimal entropy production, we simply point out that it is not a universal principle. In a separate paper,[10] we will discuss this and some of the other entropy-related stability criteria of Glansdorff and Prigogine[4] in more detail.

---

[1]E. T. Jaynes, Phys. Rev. 106, 620 (1957); 108, 171 (1957).
[2]D. N. Zubarev and V. P. Kalashnikov, Physica 46, 550 (1970).
[3]A. B. Corbet and H. Morowitz, Phys. Rev. A 6, 2298 (1972); A. B. Corbet, *ibid.* 9, 1371 (1974).
[4]P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure Stability and Fluctuations* (Wiley-Interscience, London, 1971).
[5]F. Schlögl, Z. Phys. 191, 81 (1966); 243, 303 (1971); 248, 446 (1971).
[6]I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, 3rd ed. (Interscience-Wiley, New York, 1967).
[7]R. L. Stratonovich, *Topics in the Theory of Randon Noise* (Gordon and Breach, New York, 1963 and 1967), Vols. I and II.
[8]R. Landauer, J. Appl. Phys. 33, 2209 (1962).
[9]H. Haken, Rev. Mod. Phys. 47, 67 (1975).
[10]R. Landauer, J. Stat. Phys. (to be published).
[11]B. K. Ridley, Proc. Phys. Soc. Lond. 82, 954 (1963).
[12]R. Landauer, J. Stat. Phys. 9, 351 (1973); 11, 525 (1974).