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Stability and Entropy Production in Electrical Circuits

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A number of the theorems expounded by Prigogine, Glansdorff and their collaborators are translated into electrical circuit terminology and their validity and significance discussed. The simultaneous occurrence of inductors and capacitors represents a situation not envisioned in the chemically oriented discussions and imposes some limitations. The electrical terminology also leads to "dual" theorems, in which voltage sources are replaced by current sources. The validity of the theorems in situations in which fluctuations are critical to the relaxation behavior is analyzed. The "excess entropy production" theorem is only valid if the circuit relaxation can be described by single-valued macroscopic variables, but not if it must be described by distribution functions. We stress that no purely local characterization, which examines a multistable system only in the neighborhoods where it occurs with high probability, can predict or characterize the steady state.

KEY WORDS: Electrical circuit; entropy production; stability; bistability; fluctuations.

1. INTRODUCTION

Prigogine and Glansdorff, in collaboration with a number of colleagues, have expounded, in depth, a range of theorems relating the stability of the dissipative steady state to entropy, entropy production, entropy curvature,

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etc. A good summary of this viewpoint and an accompanying citation list are found in a recent semipopular exposition.[1] The stream of work summarized in Ref. 1 is motivated largely by chemical reaction kinetics and uses language and approximations appropriate to that motivation. In this paper, we shall consider some electrical network theorems and their limitations. The electrical theorems are clearly modeled after what we shall, for brevity, call the Brussels literature.

Before deriving the detailed theorems, we shall discuss some general aspects. With the exception of Sections 5 and 6, our later discussion will concern deterministic situations, related to the macroscopic equations of motion, which will be circuit equations in our case. In the deterministic case stability questions can be answered directly from these equations of motion and we see little need for rewording these in terms of quantities that are important in thermodynamics. We only do so because it has become fashionable in the physical chemistry literature.

There is an important distinction between the Brussels literature and some of this author's past work. In the Brussels work, entropy is generally taken to be what we shall, for the sake of emphasis, call a "dead" entropy. It is an entropy found by integrating the local entropy density. The latter is taken to be the entropy of the *equilibrium state* under static parameters corresponding to those found in the reaction. Thus this "dead" entropy makes no allowance for the tightness of control maintained by the ongoing reaction. In other words the "dead" entropy is the entropy immediately after activating energy sources for an ongoing process have ceased to function, but before the system has had a chance to relax its spatial distribution of composition, pressure, temperature, etc. By contrast, this author has invoked a viewpoint in which entropy is taken to be a measure of the statistical distribution *while the dynamic process is active*, and while this process controls the fluctuations. These "live" fluctuations need not be identical to those found for the same parameters in equilibrium. This follows, perhaps, most clearly from the discussion of entropy given by McNeil and Walls[2] for a reaction beyond its critical point. For large systems where a reaction (or other kinetic process) proceeds in a spatially homogeneous fashion, so that only a minute fraction of the degrees of freedom are directly related to the progress of the reaction, the distinction between "live" and "dead" entropy may be unimportant. "Live" entropy was found useful by this author in a 1962 paper[3] calculating the transition rate between a metastable state and a stable state, over an intervening improbable state, in a dissipative system far from equilibrium. In that paper it was shown that the transition rate over the barrier takes the same form as for a particle in an overdamped bistable potential well if the "live" entropy is used to define an equivalent free energy of activation. More recently[4] it has been shown that the "live" entropy

permits generalizations of $dQ = T\,dS$ to nonequilibrium systems. In connection with this discussion of "dead" vs. "live" entropy it is appropriate here to refer to the work of Schlögl, which is intermediate in character. Schlögl's early work[5] starts from a general statistical mechanics framework, taking S to be a sum over the microstates i of a dissipative system: $S = -k \sum_i p_i \log p_i$. This is clearly a "live" entropy. In later treatments,[6,7] however, Schlögl introduces the *assumption* that the $\log p_i$ are linearly related to the macroscopic variables, and it is this author's belief that this assumption is not always consistent with the behavior of a "live" entropy. It is through this assumption that Schlögl arrives at results identical to those of the Brussels work.[2]

An electrical viewpoint has several advantages. The simplicity of electrical networks is characterized by the fact that the Onsager relationships, which normally result from a sophisticated discussion invoking detailed balance, are a simple algebraic result in network theory. In electrical engineering it has furthermore long been customary to consider voltage sources and current sources on a par, and we shall see this will result in several "dual" theorems. By contrast, in the Brussels literature, as in most transport theories, including those of solid state physics, "forces" are given an elevated role as causative agents, and fluxes are usually considered a consequence. In a field unconnected to this paper, and related to electron transport in metals,[8] the author also found it useful to invoke a viewpoint in which the fluxes entering the system are taken to be the determining boundary conditions. Additionally, as we shall see, electrical networks permit energy storage in both capacitive and inductive forms. The storage of charges in a capacitor, at a variety of potentials, bears a close analogy to the storage of chemical energy via species in variable concentrations, at an appropriate chemical potential. The inductances, however, provide an energy storage directly related to the current or "flux" in the system, and are analogous to a kinetic energy associated with the reaction rate in a chemical system (rather than with an unrelated and more easily separable background hydrodynamic flow). Finally, we may cite the fact that stability analysis, for systems very far from equilibrium, is a long-established tradition in the electrical literature. The reader could do worse than spend a few minutes with a book from the early part of this century[9] to see how sophisticated the concepts and analysis were at that time.

Another point that threads through much of the remaining discussion is that we will be concerned with theorems related to *energy disssipation* in the circuit. Energy dissipation is, in turn, easily relatable to entropy production only if there is a single temperature applicable to all of the network components.

[2] See, however, F. Schlögl in *Cooperative Effects*, H. Haken, ed., North-Holland, Amsterdam (1974), for a more careful discussion of this author's viewpoint.

2. MINIMAL ENERGY DISSIPATION

Minimal energy dissipation theorems have had a longstanding historical role (Ref. 10, pp. 79–80). For a more detailed discussion of some of the variations on this theme, and a critical analysis of aspects other than those we shall emphasize, the reader is referred to discussions by Ziman[11] and by Keller.[12]

Consider first a circuit containing only voltage sources and linear resistors. Now consider voltage distributions in this network that deviate slightly from the steady state distribution, and as a result lead to currents that do not obey Kirchoff's current law; there is a divergence of current. The potential *drop* across the voltage *sources* is left unperturbed. Now use these perturbed voltages to calculate heat generation by simply adding the dissipation terms V^2/R for all the resistive branches. Then the total dissipation is minimal for the correct voltage distribution, satisfying KCL (Kirchhoff's current law). To prove this, let V_i be the "trial" potential at node i in the network, and let V_{i0} be the correct, unperturbed potential. The dissipation, calculated as prescribed, is $\frac{1}{2}\sum_{i,j}(V_i - V_j)^2/R_{ij}$, where the sum includes all the resistive links in the network. We then have, to first order in the variation,

$$\begin{aligned}\delta[\tfrac{1}{2}\sum_{i,j}(V_i - V_j)^2/R_{ij}] &= \sum_{i,j}(\delta V_i)(V_{i0} - V_{j0})/R_{ij} \\ &\quad - \sum_{i,j}(\delta V_j)(V_{i0} - V_{j0})/R_{ij} \qquad (1) \\ &= 2\sum_{i,j}(\delta V_i)(V_{i0} - V_{j0})/R_{ij}\end{aligned}$$

Each term δV_i is multiplied by the sum of all the resistive currents $(V_{i0} - V_{j0})/R_{ij}$ leaving the ith node. If a node is connected only to resistances, and not to voltage sources, then this sum vanishes since the unperturbed solution obeys KCL. If the ith node is connected to batteries, then let us supplement the terms in (1) multiplying δV_i through additional terms of the form $\delta V_i i_B$, one term for each battery terminal, where i_B is the battery current. A battery, however, generates a fixed potential difference and the perturbation δV at its two terminals must be identical. Thus the supplementary terms $\delta V_i i_B$, which must be added to get vanishing current sums, cancel after summation over both ends of the battery. Thus each δV_i in (1) can be multiplied by a vanishing sum of unperturbed currents and (1) vanishes. The dissipation is stationary. It is furthermore easily shown, by examining the second-order terms in the perturbation, that the dissipation is *minimal* at the solution satisfying KCL.

Up to this point the perturbed potential represents only a mathematical variation, not a meaningful physical state. Let us assume, however, that

there are capacitors tied to the nodes. Let the capacitive network be sufficiently complex so that the capacitive potential at each of the original resistive nodes is independently variable by a suitable choice of capacitive charges. [If we are representing an *RC* network that does not have that many capacitors, then let us limit the allowed voltage perturbations in Eq. (1) to those achievable through variation of the capacitive charges.] Now the perturbation can be considered to represent a real physical state, though not a steady state, in which the deviation from KCL represents current flow in and out of the capacitors. If the capacitors and resistances are all positive, such a network will always relax toward a steady state, in which KCL is obeyed and the potential distribution becomes time independent. The variational principle shows that the energy dissipation must decrease during this relaxation. Note that we need not assume linearity on the part of the capacitors.

Section 1 stressed the duality of voltage and current sources. An entirely analogous minimal heat generation variational principle for circuits using *only* current sources is easily proven. The variations under consideration now obey KCL, but the associated voltage variations (calculated from Ohm's law) need not obey Kirchhoff's voltage law (KVL), i.e., we can deviate from curl $E = 0$. Then $\sum i^2R$, summed over all resistive elements, is minimal when KVL is obeyed. The perturbed solutions can again be given a physical representation by letting the deviations in voltage from KVL be dropped across inductances in series with the resistive elements. This form of the variational principle is discussed by Jeans, both for the case of a discrete network (Ref. 13, Sections 356 and 357) and for the case of a continuous current distribution (Ref. 13, Section 384).

As has been pointed out by the author in a separate publication,[14] the simplest conceivable case that mixes the two situations conceived above, a battery across a series combination of a linear resistance and inductance, can show an increasing rate of heat generation as it relaxes toward a steady state.

The theorem for voltage sources discussed above is believed to be the analog of the minimal entropy production principle discussed, for example, by deGroot and Mazur.[15] A second minimal entropy production principle is discussed, e.g., by Nicolis (Ref. 16, p. 216). Here entropy production is taken as a quadratic function of driving forces X_i,

$$\sigma = \sum_{ij} L_{ij} X_i X_j \tag{2}$$

It is assumed that some of the X_i are prescribed. Then σ is minimal if the remaining X_i are set so that their associated fluxes $\sum_j L_{ij} X_j$ vanish. ($L_{ij} = L_{ji}$ is assumed, requiring proximity to equilibrium.) In the electrical case, setting the unspecified voltage sources so that no current flows through them is equivalent to cutting these branches open. It does not seem to this author

that this formulation is identical to the one associated with Eq. (1), though the two are sometimes (Ref. 17; Ref. 10, Chapter III) discussed as if they were one. It has, however, been pointed out to me (by G. Nicolis and independently by C. Bennett) that each of these formulations can be shown to be a consequence of the other.

3. THE GENERAL EVOLUTION CRITERION

Glansdorff and Prigogine (Ref. 10, Chapter IX) invoke a criterion with the above title to discuss situations far away from equilibrium, where the Onsager relations cannot be invoked. The basic point is

$$d_X P/dt = \sum_i j_i(dX_i/dt) < 0 \tag{3}$$

Here P is the dissipation, j_i is a flux, and dX_i/dt is the time derivative of the associated force as the state is approached under a set of fixed and externally applied forces. The notation $d_X P$ indicates that only the X time derivatives are included; the terms $(dj_i/dt)X_i$ do not appear in the sum in Eq. (3).

This theorem is easily restated in network language. Consider $\dot{\phi}_i i_{ij}$, where ϕ_i is a node potential and i_{ij} is the current from node i to node j. Then consider

$$\sum_{i,j} \dot{\phi}_i i_{ij} = \sum_i \dot{\phi}_i \left(\sum_j i_{ij} \right) \tag{4}$$

This sum must vanish, since $\sum_j i_{ij}$ vanishes, through KCL. The voltage source terms drop out; a battery current contributes to two canceling terms, coming from its two terminals. The capacitive terms are of the form $\dot{V}\, dQ/dt = C(\dot{V})^2$, where V is the voltage across the capacitor, Q is its charge, and C is the differential capacitance ($C = dQ/dV$) of a possibly nonlinear capacitor. Is C necessarily positive? Glansdorff and Prigogine (Ref. 10, p. 47) assert that the compressibility must be positive if the material, locally, is to be stable. It would be convenient here to invoke a similar assertion for the differential capacitance. We are, unfortunately, far from sure that it is obviously and inevitably correct. For a capacitor under *constant-voltage conditions*, it is undoubtedly correct. A capacitor in the interior of a complex, and possibly active, network need not be under constant voltage. We expect to discuss these questions in a separate publication. For the moment, to make progress, let us suppose, in accordance with the Brussels treatment of other degrees of freedom, that C is positive or, more generally, that $\sum V_i\, dQ_i/dt$, summed over the terminals of a multiport capacitive device, is positive definite. Thus the capacitive devices contribute positively to Eq. (4), leaving

$$\sum_k i_k(dV_k/dt) \leqslant 0 \tag{5}$$

where the sum extends over the noncapacitive elements: resistors and inductances. Equality in Eq. (5) holds only if there are no capacitors at all in the circuit. If there are no inductances, then Eq. (5) becomes a sum over the dissipative elements, and the theorem agrees with the Glansdorff and Prigogine results of Eq. (3). Note that the voltages appearing in Eq. (4) are those associated with individual internal dissipative elements, not with the externally specified voltage sources, for which $\dot{V}$ vanishes. Note furthermore that we need not assume that the circuit is limited to two-terminal devices. We can include three-terminal devices, e.g., transistors, at least to the extent that it is a good approximation to represent the transistor as a purely resistive device whose capacitances can be represented as separate external elements. In that case, however, it is necessary to retain the form used in Eq. (4) for the transistor, summing over its three terminals. No stability assumption is needed to derive Eq. (5), beyond that of positive capacitances. The circuit can contain devices with gain and negative resistances, and can be violently unstable. If inductances and capacitances are both present in the circuit, then we can have a damped oscillatory approach to a steady state, and even in the simplest underdamped series *RLC* circuit $\dot{V}i$ will change sign with time.

Once again we have a dual theorem. If a network has only current sources, then

$$\sum_k V_k(di_k/dt) \leqslant 0 \tag{6}$$

where the sum is now taken over the noninductive circuit elements. The current sources have dropped out of the summation. Equation (6) is a sum over resistances only if there are no capacitors.

Let us now derive a subsidiary version of Eq. (5). Figure 1 shows $\sum i_k \dot{V}_k$ as function of some parameter λ, which measures the distance from the steady state, at which all $\dot{V}_k = 0$. At this point in the discussion this steady state can be stable or unstable. At $\lambda = 0$, we have $\dot{V}_k = 0$, and hence

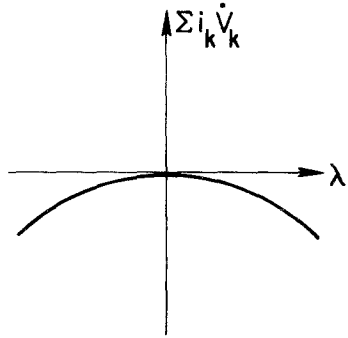

Fig. 1. $\sum i_k \dot{V}_k$ is negative, except at the steady state, $\lambda = 0$, and is continuous.

$\sum i_k \dot{V}_k$ must vanish there, while it is negative elsewhere, and is continuous. To first order in λ we then have

$$i_k = i_{0k} + \lambda i_{1k} \tag{7}$$

$$\dot{V}_k = \lambda \dot{V}_{1k} \tag{8}$$

Equation (7) follows from the fact that the steady state will not (in general) be a state of zero current. In order that

$$\sum_k i_k \dot{V}_k = \sum_k \lambda i_{0k} \dot{V}_{1k} + \lambda^2 \sum_k \dot{V}_{1k} i_{1k} \leqslant 0 \tag{9}$$

be quadratic in λ, as shown in Fig. 1, we must have $\sum i_{0k} \dot{V}_{1k} = 0$. This leaves us with

$$\sum (\lambda \dot{V}_{1k})(\lambda i_{1k}) \leqslant 0 \tag{10}$$

or

$$\sum_k \delta i_k (dV_k/dt) \leqslant 0 \tag{11}$$

where δ indicates deviations from the steady state.

Let us assume that we are given a stationary point, i.e., a point at which all $\dot{V}_k = 0$. Let us also assume that we are told that $\sum_k \delta i_k \, \delta V_k > 0$ for *all* variations away from that point. Following an argument given by Nicolis (Ref. 16, p. 233), we would then state that Eq. (11) cannot be satisfied while moving away from the stationary point, and that the point must be a point of stability. We cite this argument here without certainty about its clarity or its validity, and will rely instead upon the next section for an alternative and more broadly applicable discussion of the role of $\sum_k \delta i_k \, \delta V_k$.

4. THE EXCESS ENTROPY PRODUCTION

Consider $\sum_k \delta i_k \, \delta V_k$, summed over the dissipative elements (Ref. 10, p. 83). δi_k and δV_k are departures from a stable state. If the differential resistances dV_k/di_k are all positive, then each term in this sum is positive, and it is obvious that the sum must also be positive. Circuits with *some* negative differential resistances can, however, be stable under certain conditions.[18],[3] It therefore requires argument in that case to show that $\sum_k \delta i_k \, \delta V_k$, summed over the resistive elements, is still positive. The deviations from the steady state will decay (if there is stability) in accordance with the linearized circuit equations. The decay is then determined by the equations of a linear network,

[3] See especially the discussion associated with Fig. 2 of Ref. 18.

and is characterized by a series of characteristic values with real parts giving decay. In other words, we have

$$\begin{pmatrix} \delta i_k \\ \delta V_k \end{pmatrix} = \sum_i A_i \begin{pmatrix} \delta i_{k,i} \\ \delta V_{k,i} \end{pmatrix} e^{-\lambda_i t} \tag{12}$$

where R.P. $\lambda_i > 0$, and A_i measures the contribution of the characteristic mode i. The circuit elements are denoted by the index k. In the stable *linearized* circuit, however, power flow must clearly be out of the reactances into the resistances, and therefore these must exhibit a net dissipation. (At this point we must once again assume positive capacitances and positive inductances. A negative reactance gains energy while its excitation disappears.) Since i_k and V_k are the currents and voltages in the linearized circuit, we have

$$\sum_k \delta i_k \, \delta V_k > 0 \tag{13}$$

Conversely, if (13) is satisfied for *all* states near a given steady state of uncertain stability, that steady state must be stable. If (13) is satisfied for all of the neighborhood, then exponentially growing modes, in which energy is fed into the linearized reactances, are ruled out.

Let us specialize to the case where the linearized circuit has only positive inductances and resistances, or else has only positive capacitances and resistances. Then the linearized network yields first-order differential equations and the λ_i must all be real, leading to a simple relaxation behavior without oscillation. Now the various decay modes contributing to (13) must decay independently; the dissipation cannot depend on any interaction between them. Thus, invoking the notation of Eq. (12), we have

$$\sum_k \delta i_k \, \delta V_k = \sum_{i,k} A_i^2 \, \delta i_{k,i} \, \delta V_{k,i} \, e^{-2\lambda_i t} > 0 \tag{14}$$

For each mode, however, time derivatives are simply given by a multiplication by $-\lambda_i$; hence

$$\begin{aligned} \sum_k \left(\frac{d}{dt} \delta i_k \right) \delta V_k &= \sum_k \delta i_k \left(\frac{d}{dt} \delta V_k \right) \\ &= \sum_{i,k} -\lambda_i A_i^2 \, \delta i_{k,i} \, \delta V_{k,i} \, e^{-2\lambda_i t} \end{aligned} \tag{15}$$

The original contribution of *each* mode to Eq. (14) is positive. Thus after multiplication by $-\lambda_i$ each mode contribution becomes negative. Thus

$$\sum_k \frac{di_k}{dt} \delta V_k = \sum_k \delta i_k \frac{dV_k}{dt} < 0 \tag{16}$$

Let us compare Eq. (16) to Eq. (11). Equation (11) did not presuppose that the steady state had to be stable, whereas Eq. (16) applied near a stable steady state. Near a stable state Eq. (16) includes both Eq. (11) and its "dual," which we did not bother to discuss. Note, however, that Eq. (16) is more generally applicable. Equation (11) was derived from Eq. (5), which applies to circuits without inductances and without current sources. Both inequalities in Eq. (16) however, apply simultaneously to a circuit with an arbitrary mixture of current and voltage sources, as long as the circuit contains only one type of reactance.

The normal mode viewpoint utilized above makes it easy to emphasize an important limitation in the criteria discussed in this section. They are all inequalities that hold if we are relaxing toward a stable steady state. On the other hand, if (13), for example, is satisfied at a particular time by a particular state near a state that satisfies $dV/dt = 0$ for all its circuit elements, that does not guarantee relaxation toward a stable state. A state that satisfies $dV/dt = 0$ can have a mixture of stable and unstable modes of deviation. If we start initially with a state that includes primarily the stable modes with a very small admixture of the unstable modes, then (13) will be satisfied initially, and will only be violated after the unstable modes have grown enough to become significant.

5. NONDETERMINISTIC BEHAVIOR

The discussion up to now has concentrated on aspects related to the macroscopic equations, without allowance for fluctuations. Let us now consider more complex situations, where fluctuations are essential to a proper description of stability. We are particularly concerned with multistable systems. Transitions induced by fluctuations are needed to describe the relaxation from a metastable steady state over an intervening improbable state to a more favored steady state. Such systems were discussed in the analysis of tunnel diode circuits[3] and in a later analysis of degenerate parametric oscillators.[19] Very recently similar theories have appeared for bistable chemical systems.[20,21] The tunnel diode circuit, invoked in some of this author's earlier papers as a sample circuit, is shown in Fig. 2. Consider now what happens if we change the battery voltage from E_B to a new voltage E_B'. Each of the two stable states will be displaced, but at the same time their relative probabilities of occupation will change. If the system is given enough time, there will be fluctuation-activated transitions from the neighborhood of one stable state to that of the other.

First consider the evolution criterion of Section 3, $\sum i_k \dot{V}_k \leqslant 0$, which invokes summation over the lossy elements in the circuit. The derivation we have given applies in the presence of fluctuations. We can apply the equations

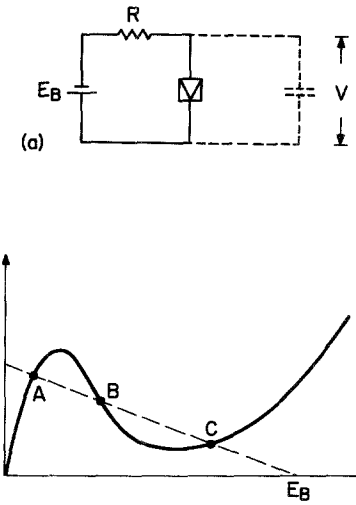

Fig. 2. Tunnel diode, with a shunt capacitance, fed through series resistance R from voltage source E_B. The solid line gives tunnel diode current as a function of V. The dashed "load line" gives the resistive current $(E_B - V)/R$. A and C are locally stable states, C is unstable.

to an individual circuit in the presence of its fluctuations, or else all of the currents and voltages can be taken to be ensemble averages. (The fluctuations must, however, be sufficiently limited to avoid negative capacitance ranges, in case these exist.)

The evolution criterion, of course, does not help us avoid the complex calculations of Ref. 2. The criterion does not permit us to predict whether we do have the correct probability distribution between the two favored states, or in which direction that distribution has to shift. After all, the only physics that went into the derivation of the criterion, beyond KCL, is that capacitances are positive. We can hardly expect any serious predictive capability from that.

It will, in fact, be instructive to consider what the evolution criterion states for Fig. 2. It tells us

$$i_R \, dV_R/dt + i_D \, dV_D/dt < 0 \tag{17}$$

where R and D denote the resistance and diode, respectively. For a fixed value of E_B, $dV_R/dt = -dV_D/dt = -dV_C/dt$, where C denotes the capacitance. Hence (17) becomes

$$(i_R - i_D) \, dV_C/dt > 0 \tag{18}$$

Noting that i_C, the capacitive charging current, is given by $i_R - i_D$, we regain

$$i_C \, dV_C/dt > 0 \tag{19}$$

which clearly tells us nothing about the real kinetics in the circuit.

What about the "excess entropy production" of (13), $\sum \delta i_k \, \delta V_k$, summed over all dissipative elements? For a *single* system in the presence of fluctuations this clearly does not have to be positive. In the presence of fluctuations, energy (even when we are at, or close to, equilibrium) can occasionally flow in the wrong direction, out of the resistors, into the energy-storing elements. As an average, over an ensemble of independently fluctuating systems, it becomes a more complex question, which we will discuss in detail. Let $\langle\ \rangle$ denote ensemble averaging. From KCL, we have for each node in a circuit

$$\sum_j \langle \delta i_{ij} \rangle = 0 \tag{20}$$

Then, multiplying by the node potential deviation δV_i and summing again, we obtain

$$\sum_{i,j} \delta V_i \langle \delta i_{ij} \rangle = 0 \tag{21}$$

We can then ensemble-average again, leaving

$$\sum_{i,j} \langle \delta V_i \rangle \langle \delta i_{ij} \rangle = 0 \tag{22}$$

Equation (22) can be written as a sum over all circuit branches

$$\sum \langle \delta V \rangle \langle \delta i \rangle = 0 \tag{23}$$

where δV is now a deviation in voltage drop from a steady state. Current and voltage sources drop out of Eq. (23) since in each case one of the factors in Eq. (23) will vanish. For capacitors $\delta i = i = C(V)\, dV/dt$. For inductors $\delta V = V = L(i)\, di/dt$. Thus Eq. (23) becomes

$$\sum_R \langle \delta V \rangle \langle \delta i \rangle = -\sum_C \langle \delta V \rangle \langle C(V)\, dV/dt \rangle - \sum_L \langle \delta i \rangle \langle L(i)\, di/dt \rangle \tag{24}$$

where R, C, and L denote the type of circuit element in the summation. Let us assume for the moment, as in Section 3, that C and L are positive. To show that the excess entropy production principle does not apply generally, it will be adequate to consider the simpler case $C(V) = \text{const}$, and to give a counter example applicable to that case, without inductances. The right-hand capacitive term in (24) will be positive if $\langle \delta V \rangle$ and $\langle dV/dt \rangle$ are opposite in sign. Are they?

Consider the circuit of Fig. 2. Now increase E_B, but stay within the range of bistability. Keep the system at the new battery voltage long enough to permit the rapid relaxation that takes place near each of the two locally stable states. Let us not, however, stay there long enough to permit the slower transitions from the low-voltage branch (A) to the high-voltage branch (C), which would eventually take place.[2] Then reduce E_B slightly again, but not nearly as much as the original increase. We have now created the state for which we want to compute $\langle \delta V \rangle \langle dV/dt \rangle$ as the relaxation proceeds. Just after arriving at this final state we will at first again have a

rapid local adjustment which initially dominates $\langle dV/dt \rangle$, and is negative, corresponding to the final reduction in E_B. What about $\langle \delta V \rangle$? It represents the voltage deviation from the final steady state. It will be dominated by the large voltage jumps from one branch to the other that still have to take place. Since almost none of these have taken place, and since the overall change in E_B was an increase, $\langle \delta V \rangle$ is negative. Thus it has the same sign as $\langle dV/dt \rangle$ does, initially, and "excess entropy production" fails.

6. IMPOSSIBILITY OF ANY LOCAL STABILITY CRITERION

It has been argued in Ref. 14 that no criterion considering only the behavior in the neighborhood of states A and C of Fig. 2 can make predictions about relative probability distributions between these two neighborhoods. Since Ref. 14 concentrated on a mechanical model, let us here argue for the same point using, in consistency with the rest of this paper, an electrical circuit. Instead of utilizing the circuit of Fig. 2, we will invoke the slightly different circuit of Fig. 3. Here the series resistor has been replaced by a thermionic diode. The exact choice of device is not important; the key point is that this is a device that, in contrast to the resistor of Fig. 2, transfers one whole electron at a time. In that case we have a circuit whose master equation can be solved very simply.[3,20–22] Let $W_{N+1,N}$ give the probability of a transition from the state with N electrons on the upper capacitor plate to one with $N + 1$ electrons, and let $W_{N,N+1}$ be the inverse transition probability. In the steady state, then, the respective occupation probabilities obey $\rho(N + 1)/\rho(N) = W_{N+1,N}/W_{N,N+1}$. Thus the relative probabilities of

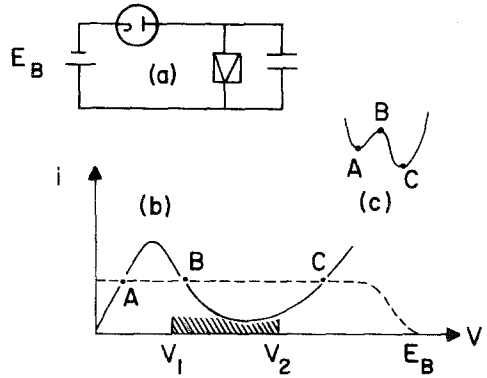

Fig. 3. (a) The circuit and (b) its characteristic. A tunnel diode (solid characteristic) is shunted by a capacitance and in series with a device (dashed load line) that transfers one electron at a time. (c) An analogous unsymmetric bistable potential well, in which C is arbitrarily drawn as the preferred state, which need not be the case for (b). The range between V_1 and V_2 in (b) illustrates a possible range of operation for the "auxiliary circuit" invoked in the text.

occupation of any two states $\rho(M)/\rho(N)$ can be found by multiplying all the intervening ratios of the form just given.

Our basic point: We shall show how to modify a system shown in Fig. 3 in such a way that the system behavior and all the local properties near states A and C remain unaffected, but still change the kinetics over a range of the intervening states. Thus we can change $\rho(\mathrm{C})/\rho(\mathrm{A})$, without changing the entropy associated with either C or A, and without changing any of the time or q 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 kinetics along the whole path connecting C and A must be involved.

Let us now describe such a modification for Fig. 3. Let the capacitor consist not only of the intrinsic device capacitance but, in addition, let there be a parallel external capacitor. The plates of this external capacitor are connected to springs and the plates attract each other as the capacitor is charged. (This results in an inevitable capacitive nonlinearity; that is an incidental point not bearing on our argument.) Now as the capacitor plates move between the positions corresponding to V_1 and V_2 in Fig. 3b, the capacitor plate motion is used as a switch to connect an auxiliary circuit between the two plates. This auxiliary circuit is then active only between V_1 and V_2 and modifies the kinetics in that range. The simplest example of an auxiliary circuit would be a very large resistance at a very high temperature. The large value of resistance ensures that the macroscopic or average behavior of the circuit, as given by the equations of motion, remains unaffected. The high temperature, however, means that fluctuations in the capacitive charge are raised, increasing both $W_{N,N+1}$ and $W_{N+1,N}$ similarly, and thus bringing the ratio $\rho(N+1)/\rho(N)$ closer to unity. This flattens the probability distribution within the "noisy" range, and thus brings $\rho(q_1)/\rho(q_2)$ closer to unity (q_1 and q_2 are the capacitive charges corresponding to V_1 and V_2). To make this argument a very clean one, we should preserve the nature of our capacitive charge ladder, which only allows charge transitions by an electronic charge. To satisfy this requirement, the resistor in the auxiliary circuit would, for example, be made up of a diode (thermonic or tunnel) or of two diodes in parallel and facing in opposite directions. Outside of the range of the auxiliary circuit $\rho(N+1)/\rho(N)$ remains unchanged. Thus by "leveling" the variation of ρ in the range between q_1 and q_2 we have changed $\rho(\mathrm{C})/\rho(\mathrm{A})$. (We need not restrict ourselves to a comparison of the bistable circuit with and without auxiliary circuit. Compare, instead, two situations with the same auxiliary apparatus, and only change the intensity of the noise source between the two comparison cases.)

Some auxiliary discussion of further details at the switch points V_1 and V_2 is appropriate. Let us specialize to the case in which the capacitor plate positions adjust rapidly compared to the typical time between electron transitions. Furthermore assume that the value V_1 is achieved when there are

more than N_1 electrons on the capacitor, but less than $N_1 + 1$. Thus $W_{N,N+1} \gg W_{N+1,N}$ and the steady state probability density drops as we enter the noisy range. There is, however, a comparable rise as we leave the noisy range at V_2, which is assumed to occur between N_2 and $N_2 + 1$ electronic charges. More explicitly, multiplying the ratios specifying $\rho(N + 1)/\rho(N)$ we find

$$\rho(N_2 + 1)/\rho(N_1) = (W_{N_1+1,N_1}/W_{N_2,N_2+1})\gamma, \tag{25}$$

with

$$\gamma = \prod_{N_1+1}^{N_2} (W_{N_i+1,N_i}/W_{N_i-1,N_i}) \tag{26}$$

By going to a sufficiently noisy system, γ can be brought as close to unity as desired.

The discussions in this section relate to the significance of first-order transitions in dissipative steady state systems. Consider a bistable system that is slowly modulated by subjecting it to a change in temperature, battery voltage, or some other parameter. As this change takes place, assume that the more likely state becomes the less likely state, but still remains as a metastable state. That is a first-order transition. In a system of limited size it is not discontinuous, but consists of a gradual change in the two relative probabilities. The point at which the two probabilities are equal may be considered the transition point or phase equilibrium point. The observed transitions will exhibit a hysteresis and will take place above or below this transition point, depending on the direction of the parameter change. The size of the hysteresis depends upon the rate at which the parameter is modulated. Note that in accordance with our conclusions about the inadequacy of local criteria, the parameter that corresponds to the first-order phase equilibrium cannot be determined without concern for the phase transition mechanism. *Phase equilibrium can no longer be regarded as a thermodynamic coincidence, determined by the equality of free energies, as in the case of an equilibrium transition.*

7. SOME KEY POINTS

The "evolution criterion" $d_X P/dt > 0$ is valid for circuits with voltage sources, resistances, and capacitors, and with no inductances. The differential capacitances have to be positive. The theorem applies even in the presence of pronounced fluctuations. It has no direct relation to circuit stability.

The "excess entropy production" theorem $\sum_k \delta I_k \, \delta V_k > 0$ is a result of stability, but does not guarantee stability unless satisfied for *all* states in the neighborhood of the test state, as is made quite clear in the original Brussels discussions. It applies to a circuit with any mixture of reactances and with a mixture of current and voltage sources. The differential resistances need not be positive, as long as overall circuit stability is maintained. The theorem fails to

apply to an individual circuit in the presence of fluctuations. The theorem fails to apply to a circuit whose relaxation behavior must be described by distribution functions, rather than single-valued macroscopic quantities.

All of the theorems are really heat generation theorems, rather than entropy production theorems, if the circuit elements are at different temperatures.

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