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$dQ = T\,dS$ far from equilibrium

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It has been pointed out that heat flow in the slowly modulated dissipative steady state in some circuits far from equilibrium obeys a relationship $dQ-dQ_0 = T_N\,dS$. dQ_0 is the heat flow calculated in a macroscopic way by multiplying the ensemble averages of currents and voltages for the dissipative elements. T_N is the temperature characterizing the fluctuations in the degree of freedom under consideration. S is the entropy defined in the usual statistical-mechanical fashion. This relationship is illustrated through a particularly simple example: The divergent heat flow into a circuit as a second-order transition is approached from the high-symmetry side. The general case is more complex and discussed subsequently, with special attention to the complications caused by asymmetric distribution functions, and the fact that the dissipation in slowly shifted steady state differs from that in the exact steady state. The relationship, expressed in a form which involves entropy changes, is valid only if the distribution functions in the dissipative case mimic equilibrium distribution functions very closely. Other forms have a much broader applicability.

INTRODUCTION

The statistical mechanics of the dissipative steady state far from equilibrium has received considerable attention in recent years and we can cite only a few of many important recent contributions.[1-5] This author's work, starting[6] in 1961, has emphasized questions concerning the relative stability of "... *structures* which are in a steady (time-invariant) state, but in a *dissipative* one, while holding on to information," (italics added). A recent paper[7] distinguishes between relative stability questions in small and large systems.

Much of the recent work[1-6] emphasizes the frequent, though by no means universal, analogies between open dissipative systems and systems closer to equilibrium. Thus, first- and second-order phase transitions, with all their concomitant symptoms such as hysteresis, nucleation, soft modes, critical fluctuations, etc., can occur in the open system. In this paper, we discuss heat flow in the slowly modulated open system and exhibit further analogies which, so far at least, have been discussed only by this author.

When we take a system very slowly through a sequence of states, each approximating equilibrium, then the relation $dQ = T\,dS$ tell us that the heat flow into the system, from the thermal reservoir, is related to the changes in the system's spread in phase space, as measured by dS. At first sight, one would hardly expect to invoke $dQ = T\,dS$, *with an equality sign*, if the set of states represent steady states far from equilibrium. It has been pointed out, however, that with very simple generalizations of the definitions of T and dQ, $dQ = T\,dS$ can in fact remain valid far from equilibrium.[8-10] Our discussions of the range of validity for the generalized version of $dQ = T\,dS$, and of the degree of approximation involved, are complex. We shall first discuss a simple example which will avoid most of the complexities of the later more general case.

I. SIMPLE EXAMPLE: APPROACH TO BIFURCATION

Consider the tunnel-diode circuit shown in Fig. 1(a), involving two negative-resistance devices and two capacitors, which will be taken to be linear. Instead of a tunnel diode, any purely resistive two-terminal device having the same sort of negative-resistance characteristic as is shown in the solid curve in Fig. 1(b), can be used. As the applied voltage is increased beyond that shown in Fig. 1(b) a second-order transition takes us from the monostable region of Fig. 1(b) to a bistable regime illustrated in Fig. 1(c). (For some shapes of the characteristic more complex behavior is possible.) As the transition is approached from the monostable regime, the distribution function for the capacitive charge becomes broad. We shall show that this broadening gives rise to a contribution to the heat flow into the circuit, from the thermal reservoir.

Consider an ensemble of independently fluctuating circuits, in which E_B is increased slowly toward the bifurcation threshold E_T. For each member of the ensemble $E_B i_B = \sum Vi$, where the sum extends over all circuit elements and $E_B i_B$ represents power flow out of the battery. After ensemble averaging we find

$$\langle E_B i_B \rangle = \sum_{R,C} \langle Vi \rangle , \tag{1.1}$$

where the subscripts R and C denote the resistive and capacitive elements, respectively. Conservation of power, however, also applies to the ensemble averages which enter into the macroscopic-

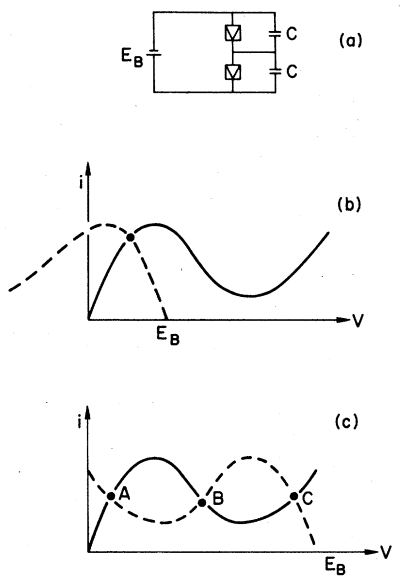

FIG. 1. (a) Tunnel-diode circuit. (b) Characteristics for monostable regime. Solid line gives current through lower diode as a function of voltage V at point between the two diodes. Dashed line gives current through upper diode as a function of the same midpoint voltage. (c) Bistable regime under larger voltages, A and C are stable states, B is unstable.

circuit equations:

$$\langle E_B\rangle\langle i_B\rangle = \sum_{R,C}\langle V\rangle\langle i\rangle . \tag{1.2}$$

If Eq. (1.2) is not considered obvious, it can be derived by a few lines of algebra contained in Ref. 9 and repeated in Sec. II. Since E_B does not fluctuate, the left-hand side (lhs) of Eqs. (1.1) and (1.2) are identical. Subtracting the two equations and rearranging terms leaves

$$\sum_C (\langle V_C i_C\rangle - \langle V_C\rangle\langle i_C\rangle) = -\sum_R (\langle V_R i_R\rangle - \langle V_R\rangle\langle i_R\rangle). \tag{1.3}$$

The right-hand side (rhs) of Eq. (1.3), after multiplication by a time element dt can be written as $dQ - dQ_0$. dQ is the ensemble-average heat flow from the reservoir into the circuit, whereas dQ_0 represents that heat flow calculated from the macroscopic-circuit equations. $dQ - dQ_0$ is, therefore, the interesting heat flow, above and beyond the obvious dissipation associated with the sequence of states being traversed. The lhs of Eq. (1.3), after multiplication by dt, is analogous to the term dU-$p\,d\tau$ (τ is volume) in the analysis of a compressible gas, and will be written as dU-dU_0. Thus, Eq. (1.3) becomes

$$dU - dU_0 = dQ - dQ_0 . \tag{1.4}$$

$dU_0 = \sum_C \langle V\rangle\langle dq\rangle$ is not, in general, a perfect differential. If, however, the capacitors are linear, then $\langle V\rangle = C\langle q\rangle$ and U_0 is just the capacitive energy associated with the average charge. Thus, below the bifurcation threshold, where the charge distribution fluctuates about a symmetrical voltage distribution, U_0 is $\frac{1}{4}CE_B^2$. The average energy U is higher because the charge distribution fluctuates. If q is the total charge which has come into the midpoint junction between the two capacitors from the tunnel diodes, elementary capacitive-energy considerations yield

$$U - U_0 = \langle q^2\rangle/4C . \tag{1.5}$$

q is subject to stochastic fluctuations about its zero average value. As has been discussed elsewhere[11] the fluctuations in q can be described by

$$j = \rho v(q) - D\frac{\partial \rho}{\partial q} , \tag{1.6}$$

where j is the flux of probability, v is the velocity $\dot{q}$ toward $q = 0$ given by the circuit equations, and the final rhs diffusion term represents noise. This term permits ensemble members initially at the same value of q to separate later. The diffusion coefficient D can be expressed in terms of the shot noise in the tunnel diode.[12] The only important point for our present purposes is that D is a smoothly varying function of diode voltage, and does nothing dramatic near the peak of the tunnel-diode characteristic, i.e., at the threshold voltage E_T. As discussed in Refs. 11 and 12, the replacement of a master equation which treats discrete electronic jumps by the continuous approximation of Eq. (1.6) is justified near the points of local stability (where ρ changes least rapidly) if the system is not so small that even one electronic charge changes ρ appreciably. Even in that case, however, it is only the exact form of our subsequent equations that changes, and not their qualitative or physical content. In the steady state, j in Eq. (1.6) vanishes and upon integration this leads to

$$\rho = A\exp\left(\int \frac{v}{D}\,dq\right) . \tag{1.7}$$

Here $v = -q/\tau$, where τ is the circuit relaxation time for restoration to the macroscopic solution $q = 0$. $\tau = RC$, with R the differential diode resistance, which goes to infinity as the threshold voltage E_T is approached and as the point of intersection of the two characteristics in Fig. 1(b) approaches the peak current. If $\delta = E_T - E_B$ then $R = 2\delta^{-1}(d^2I/dV^2)^{-1}$, where d^2I/dV^2 is the curvature at the peak of the tunnel-diode characteristic. Thus, $\tau \sim \delta^{-1}$ and we shall simply write $\tau = \alpha/\delta$. Substituting $v = -q/\tau$ and $\tau = \alpha/\delta$ in Eq. (1.7) yields

$$\rho = A\exp(-q^2\delta/2\alpha D) . \tag{1.8}$$

Thus, the distribution becomes broad as $\delta \to 0$. As in other critical phenomena, as δ becomes very small, the relation $v = -q/\tau$ should be supplemented by higher-order terms in q. This, in turn, will limit the broadening of the distribution function.

The distribution function of Eq. (1.8) substituted in Eq. (1.5) yields

$$U - U_0 = \alpha D/4\delta C . \tag{1.9}$$

Eq. (1.9) substituted in Eq. (1.4) gives

$$dQ - dQ_0 = -(\alpha D/4\delta^2 C)\, d\delta . \tag{1.10}$$

Note that dQ_0 has no anomalies, as the threshold is approached. Thus, Eq. (1.10) gives a divergent heat flow into the circuit as the transition is approached, reflecting the broadening of the distribution function in Eq. (1.8). Note that $dQ - dQ_0$ is a reversible heat flow. If $d\delta$ is reversed, so is the heat flow.

The distribution function in Eq. (1.8) is of the form $\exp(-U/kT_N)$, if we take T_N to be $2\alpha D/4Ck\delta$. T_N is the equilibrium temperature which would give the same capacitative fluctuations as are observed in the dissipative circuit. We can also use Eq. (1.8) to define an entropy, $S = -k\int \rho \ln \rho \, dq$. It is then easily shown that the heat flow given in Eq. (1.10) obeys

$$dQ - dQ_0 = T_N \, dS . \tag{1.11}$$

Equation (1.11) is based on the fact that the distribution function in the active circuit has exactly the same form as an equilibrium distribution function. This will break down, for example, if we go beyond the relationship $v = -q/\tau$, and include higher-order terms. Thus, Eq. (1.11), as an exact relationship, is of limited validity. Eq. (1.10), however, can be written in the form

$$dQ = dQ_0 + dQ_r . \tag{1.12}$$

dQ_0 is the irreversible heat flow calculated from the ensemble averages. dQ_r is a reversible heat flow associated with the dispersion in the ensemble, and equals $dU - dU_0$. Eq. (1.12) is much more broadly applicable than Eq. (1.11).

This example has been selected partly because of its general physical interest, but also, as already stated, because it avoids many of the complexities of the more general case. A second point: Our results are based on the distribution function of Eq. (1.8), associated with a temperature T_N, which can be very different from the ambient temperature. Within the "local equilibrium" approximation typical in the physical-chemistry literature[13] it would not have been possible to derive our result.

One of the key differences between chemical systems and electrical systems: A circuit description makes it easy to focus on a few essential degrees of freedom that are intimately related to the ongoing dynamic process. Thus, charge fluctuations in a capacitor are obviously determined by the noise generated in the circuit and have, at best, a very indirect connection to the ambient temperature. By contrast, in discussing chemical kinetics we are likely to mask the entropy contribution of the fluctuations related to the progress of the reaction with the entropy of the huge number of unimportant degrees of freedom. This leads to a "local equilibrium" assumption.

Finally, we ask whether there are systems in which our divergent heat flow can actually be measured. We are concerned with the entropy changes in only a single degree of freedom, and a heat flow whose divergence cannot follow Eq. (1.10) all the way as $\delta \to 0$. Furthermore the system must be modulated slowly compared to its relaxation time, and that relaxation time itself becomes long as $\delta \to 0$. Then, the divergent heat flow must be measured against the continuing background of the uninteresting term dQ_0. If, instead of a single system, we invoke a great many similar small systems, then we must take care to look at these systems together as far as their modulation parameter is concerned, but not as far as their fluctuations are concerned. All this means that actual measurement may prove to be very difficult. We now proceed to the more general case.

II. ENERGY-FLOW EQUATION

Consider an ensemble of circuits subject to independent fluctuations through their contact with the thermal reservoir. Assume that at some time in the distant past these ensemble members were all in the same state, but have become separated through their differing history of fluctuations. (Any other method of defining an ensemble corresponding to our intuitive notion of a set of circuits following the same noiseless macroscopic equations of motion is likely to be equally satisfactory.) We shall assume that the voltage and current sources are fixed, and not subject to fluctuations. Let us furthermore, for notational simplicity, restrict ourselves to two-terminal devices. That, however, is only a pedagogic device. As long as the multiport devices do not mix circuit types, they do not represent a real complication.

Denote the current from node i of the circuit, to node j by i_{ij}; the potential at i by V_i, and $V_i - V_j$ by V_{ij}. If i and j are not connected nodes, i_{ij} will be taken as zero. Note that i_{ij} and V_{ij} are both odd under exchange of i and j. We will show that

$$\sum_{i<j} \int_{t_1}^{t_2} [\langle V_{ij} i_{ij} \rangle - \langle V_{ij} \rangle \langle i_{ij} \rangle] \, dt = 0 \tag{2.1}$$

for any time interval (t_1, t_2). From the conservation of current, we have, for any node i,

$$\sum_j i_{ij} = \sum_j i_{ji} = 0 . \tag{2.2}$$

Multiplying Eq. (2.2) by an arbitrary parameter ϕ_i, which is a function only of the node involved, and then summing over the index i, yields $\sum_{i,j} \phi_j i_{ij} = 0$. Similarly, $\sum_{i,j} \phi_j i_{ij} = 0$. Hence,

$$\frac{1}{2} \sum_{i,j} (\phi_i - \phi_j) i_{ij} = 0 . \tag{2.3}$$

To derive Eq. (2.1), first we take $\phi_i = V_i$ in Eq. (2.3) and then take an ensemble average. Subsequently, we take $\phi_i = \langle V_i \rangle$ in Eq. (2.3) and again ensemble average. Subtracting the two equations yields Eq. (2.1). Note that nonfluctuating sources of voltage and current sources contribute equally to $\langle V_{ij} i_{ij} \rangle$ and to $\langle V_{ij} \rangle \langle i_{ij} \rangle$ and therefore can be dropped from the expression (2.1).

To illustrate the significance of Eq. (2.1), we consider the simple circuit shown in Fig. 2. Eq. (2.1) can be written

$$\int_{t_1}^{t_2} (\langle V_C i_C \rangle - \langle V_C \rangle \langle i_C \rangle) \, dt$$

$$= - \sum_{i=1,2} \int_{t_1}^{t_2} (\langle V_{R_i} i_{R_i} \rangle - \langle V_{R_i} \rangle \langle i_{R_i} \rangle) \, dt , \tag{2.4}$$

where the subscripts identify the capacitor and the two resistances, respectively. The lhs of (2.4) is the difference between the ensemble average of the energy put into the capacitor and this energy as calculated from ensemble averages.

Let us rewrite Eq. (2.4) in the form

$$U_F(t_1, t_2) = Q_F(t_1, t_2) , \tag{2.5}$$

where U_F denotes the stored-energy terms on the lhs of Eq. (2.4), and Q_F denotes terms related to heat flow from the thermal reservoir into the resistor. The subscript F reminds us that we are dealing with fluctuating ensembles; if there is no statistical spread in the current and voltage distributions then $U_F = Q_F = 0$. In the steady state, power flow into the capacitor must vanish and $\langle V_C i_C \rangle = \langle V_C \rangle \langle i_C \rangle = 0$. Thus, only in the presence of a time dependence and fluctuations can Eq. (2.5) tell us anything interesting.

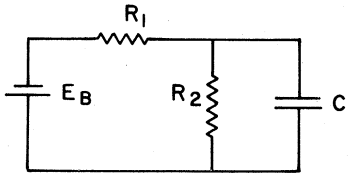

FIG. 2. Battery with two resistors and one capacitor.

We can identify terms of the type found on the lhs of Eq. (2.4) as changes in total stored energy only if we assume that the energy input to the energy-storage devices comes exclusively from electrical terminals. We must rule out external modulation of capacitors, e.g., by a mechanical force applied to the capacitor plates. [Note that this is only a condition for the interpretation of Eq. (2.4), not for its validity.] Changing battery voltages, resistor temperatures, and resistor values can, however, all be left as sources of time dependence for the circuit.

In the further discussion of the example of Fig. 2, in this section, let us restrict our attention to the case of linear resistors, generating Johnson noise, and to linear capacitors. In this case, the effects of the fluctuating emf generated in the resistors is simply added linearly to the macroscopic-circuit solution resulting from $E_B(t)$. Thus, the capacitive charge fluctuations can be calculated independently of $E_B(t)$. For the capacitor $i_C \, dt = dq$, where $q = CV_C$ is the charge on the capacitor. Thus,

$$U_F(t_1, t_2) = \int_{t_1}^{t_2} (\langle V_C \, dq \rangle - \langle V_C \rangle \langle dq \rangle) \, dt$$

$$= \frac{\langle q^2 \rangle}{2C} \Big|_{t_1}^{t_2} - \frac{\langle q \rangle^2}{2C} \Big|_{t_1}^{t_2} = \frac{\langle (q - \langle q \rangle)^2 \rangle}{2C} \Big|_{t_1}^{t_2} . \tag{2.6}$$

U_F is the energy change associated with the departures from $\langle q \rangle$, and due entirely to the fluctuations. If we assume that both resistors in Fig. 2 are at the same temperature T, and that this temperature is changed very slowly, then $\langle (q - \langle q \rangle)^2 \rangle / 2C$ must be the energy of the fluctuations of a capacitor, in equilibrium, at the temperature T. Changes in that energy must then equal $\int T \, dS$, where the entropy S of the capacitor is given by the usual expression

$$S = -k \int \rho(q) \ln \rho(q) \, dq$$

in terms of the distribution function ρ. Thus, Eq. (2.5) becomes

$$T \, dS = dQ_F . \tag{2.7}$$

Eq. (2.7) shows that entropy changes associated with the capacitive fluctuations can be calculated in the usual way from the heat energy taken up by the resistor, after subtracting out the uninteresting macroscopic-circuit dissipation terms

$$\sum_R \int_{t_1}^{t_2} \langle i_R \rangle \langle V_R \rangle \, dt .$$

Note that, in Eq. (2.6), we utilized the linearity of the capacitor, through the relation $\langle V_C \rangle = \langle q \rangle / C$.

In the more general case, we cannot express $\langle V_C\rangle\langle dq\rangle$ as a differential of a function of $\langle q\rangle$. In fact, the expression $\langle V_C\,dq\rangle - \langle V_C\rangle\langle dq\rangle$ is completely analogous to $dU - p\,d\tau$ (where τ is volume) in the analysis of a compressible gas, as pointed out in Sec. I. Thus, $\langle V_C\rangle\langle dq\rangle$ will not, in general, be a perfect differential. Note that Eq. (2.1) can be written in the form of Eq. (2.5), not just for the simple case of Fig. 2, but with complete generality. Eq. (2.1) can always be separated into terms dealing with the circuit elements which store energy, written on the lhs of Eq. (2.5), and terms dealing with dissipative elements, written on the rhs of Eq. (2.5). While Eq. (2.5) is a result of energy conservation, it includes elements that are reminiscent of $T\,dS = dQ$. The rhs as has been pointed out, represents the heat flow from the reservoir into the resistive elements, to the extent that it exceeds the amount predicted from the ensemble averages in the usual macroscopic way. Thus it is an obvious generalization of the usual dQ term in $T\,dS = dQ$. The lhs relates to a dispersion in the energy-storage terms; if all ensemble members behaved alike it would vanish. It is therefore a measure of the fluctuations in the energetic behavior, and at least in that way, representative of $T\,dS$. Note that the derivation of Eq. (2.1) did not require any assumptions about Gaussian distribution functions, detailed balance, slowly modulated systems, proximity to a steady state, etc. *Some* of these restrictions will be introduced at later stages in this paper.

III. MACROSCOPIC HEAT FLOW FOR A TIME-DEPENDENT CIRCUIT

This section will be devoted to an analysis of

$$\sum_{i>j}\int_{t_1}^{t_2}\langle V_{ij}\rangle\langle i_{ij}\rangle\,dt \tag{3.1}$$

summed over the reactive circuit elements. (For the reader who is more acquainted with chemical reactions than electrical circuits, we note that "reactive" circuit elements are energy-storing elements, i.e., capacitors and inductors, in contrast to resistors.) In this section, we will assume that we are dealing with a slowly modulated system, which is always close to a steady state. In other words some parameter, e.g., a battery voltage, changes slowly compared to the speed of relaxation of the circuit. The actual voltages and currents $[e(t),\ i(t)]$ in the time-dependent circuit will then be very close to those which would have existed if the *current* value of the changing parameter (e.g., battery voltage) had existed for a long time. Let $e_{SS}(t)$ and $i_{SS}(t)$, respectively, be the voltages and currents corresponding to the steady state for the parameter value prevailing at the time t. In the steady state, the capacitive currents and the inductive voltages will vanish. In the slowly modulated circuit, capacitive currents, for example, cannot vanish exactly. If the charge $q(t)$ on a capacitor has a slow time dependence then $i_C = dq/dt$ must be of order $1/T$, where T is the time scale over which an appreciable modulation takes place. Similarly for the inductive voltages.

If we replace our network by one in which all capacitors are removed, and all inductances short circuited, then we achieve the steady state instantaneously. Our actual state, in the modulated system, can be found by inserting small current sources, $i_C = dq/dt$, in place of the capacitors, and voltage sources, $e = -d\phi/dt$, in the short-circuited inductive links. These sources will produce small perturbations away from the exact steady state. Note that the distinction between dq/dt and dq_{SS}/dt will be second order in $1/T$, and we will, therefore, neglect this distinction. Thus, the current and voltage sources which perturb the circuit away from the exact steady-state solution can be calculated from the steady-state solutions $e_{SS}(t)$ and $i_{SS}(t)$. To avoid any possible lingering confusion $e_{SS}(t)$ and $i_{SS}(t)$ are time dependent because i_{SS} and e_{SS} are functions of the modulation parameters, and these, in turn, are time dependent. Letting the perturbations away from the steady state be denoted by $(\delta e, \delta i)$ we have

$$e(t) = e_{SS} + \delta e,\quad i(t) = i_{SS} + \delta i, \tag{3.2}$$

and for the heat dissipation

$$ie = i_{SS}e_{SS} + i_{SS}\delta_e + e_{SS}\delta i, \tag{3.3}$$

to first order in $1/T$. Let the additional heat flow due to the perturbations, $i_{SS}\delta_e + e_{SS}\delta i$, be denoted by δL. ("L" as reminder that we are calculating heat flow from a state which *lags* behind the "current" value of the steady state.) Note that δe and δi arise from the capacitive (and inductive) changes in time and thus reverse sign if the time dependence of $e_{SS}(t)$ and $i_{SS}(t)$ is reversed. Hence, δL is reversible and $\oint dL\,dt$ vanishes if the circuit is varied back and forth *along the same set of intermediate states*. It can easily be shown, however, that in more general situations $\oint \delta L dt$ does not

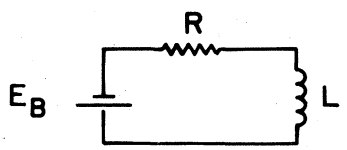

FIG. 3. Battery across resistance and inductance in series.

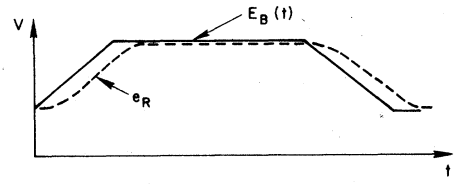

FIG. 4. E_B in Fig. 2 is a function of time. e_R, the voltage across the resistor, lags the battery voltage.

vanish; δL is *not* a perfect differential of a state function.

Finally we must emphasize that while $\delta L \sim 1/T$ and becomes very small with slow modulation, $\int_A^B \delta L\, dt$ between two fixed states A and B extends over a time T and is thus independent of the modulation rate. The integral is only a function of the exact path taken between A and B.

To make the preceding discussion of δL more meaningful, consider the circuit of Fig. 3 and assume that the battery voltage is modulated with time. Figure 4 exhibits both the time dependence of the battery voltage and of the voltage across the resistor. The latter lags the former by the relaxation time of the circuit L/R. Thus, the dissipation during the initial voltage rise is less than would be calculated from the steady state, and $\delta L < 0$. The opposite holds during the later voltage reduction, where the actual resistive current exceeds the "steady state" value of current ($=E_B/R$).

Note that if Prigogine's minimal entropy production theorem[14] were applicable to Fig. 4, δL would have to be a second order in $1/T$, and positive.

IV. REVERSIBLE AND IRREVERSIBLE HEAT FLOW

Eq. (2.1) can be written in the form

$$\sum_U \langle Vi\rangle\, dt - \sum_U \langle V\rangle\langle i\rangle\, dt = -\sum_R \langle Vi\rangle\, dt + \sum_R \langle V\rangle\langle i\rangle\, dt, \quad (4.1)$$

where the subscripts U and R denote summation, respectively, over energy-storing components and over resistive devices. Let us denote, in accordance with Eq. (2.5), the lhs of Eq. (4.1) by dU_F. The term $-\sum_R \langle Vi\rangle\, dt$ will be denoted by dQ; it is the expectation value of the heat flow *from* the heat bath into the circuit. The final right-hand term of Eq. (4.1) will be denoted by $-dQ_0$, the subscript denoting that it is calculated from the ensemble averages. Thus

$$dU_F = dQ - dQ_0. \quad (4.2)$$

We immediately see that in a steady state, not subject to modulation, $dU_F = 0$ and hence $dQ = dQ_0$. For the steady state, therefore, the actual expectation of the heat dissipation and that calculated from ensemble averages are identical.

In Sec. III we treated slowly modulated systems and pointed out that for these

$$dQ_0 = dQ_{SS} + \delta L, \quad (4.3)$$

where dQ_{SS} represents the dissipation calculated from ensemble averages in the steady state. Combining Eqs. (4.2) and (4.3) yields

$$dQ = dU_F + dQ_{SS} + \delta L. \quad (4.4)$$

In a slowly modulated system, dU_F is reversible in the same sense as was pointed out for δL in Sec. III. Energy flowing into the components when traversing a sequence of states must flow out again when traversing them in the opposite direction. (As pointed out, however, dU_F is not a perfect differential.) Thus in the rhs of Eq. (4.4) only the term dQ_{SS}, representing the steady-state dissipation, represents irreversible heat flow. In the slowly modulated system it is supplemented by two reversible terms. One of these, dU_F, relates to fluctuations, i.e., to differences within the ensemble. The other, δL, is related to the macroscopic equations.

V. CONNECTION BETWEEN dU_F AND $T\,dS$

We have already alluded to the fact that dU_F is related to ensemble dispersion. Can we relate it more specifically to entropy changes? We shall try to do this first through a very simple general argument, and later in a more detailed way. The general argument is that of Secs. I and II and starts by observing that the distribution function for some reactive circuit component, say the charge on a capacitor, in a circuit far from equilibrium, can mimic the distribution function found for some equilibrium condition. Thus, the voltage on an equilibrium capacitor can be controlled by a battery applied across it. The extent of the fluctuations in the capacitive charge and voltage can be controlled by the temperature of a resistor in series with the battery and capacitor. If the two distribution functions (that for the capacitor in the equilibrium circuit and that for the capacitor in the dissipative circuit) are identical then the entropy

$$S = -k \int \rho \ln \rho\, dq \quad (5.1)$$

for the two distribution functions must also be identical. The fluctuations on the capacitor in equilibrium are characteristic of the resistor temperature. We can, therefore, associate the distribution function with that temperature, and use it as an "effective" temperature for the nonequilibrium cir-

cuit. An observer of the capacitive fluctuations, unaware of the remaining circuit, would assign that temperature to the capacitor. This temperature has little relation to the ambient temperature, i.e., the physical temperature of the capacitor plates, and is instead determined by the noise in the electrical circuit.

Let us now assume, as we modulate a nonequilibrium circuit, that the distribution function for a given reactance mimics a series of successive equilibrium distribution functions. For the equilibrium sequence we have

$$dU - \langle V\rangle\langle i\rangle\,dt = T\,dS\,. \tag{5.2}$$

Here, dU is the energy change of the reactance, $\langle Vi\rangle\,dt$. T can itself be changing as the modulation proceeds. Let us denote $\langle V\rangle\langle i\rangle\,dt$ by dU_0, in analogy to our earlier definition of dQ_0. Thus Eq. (5.2) becomes

$$dU - dU_0 = T\,dS\,. \tag{5.3}$$

Since, however, the distribution functions for the sequence of equilibrium states are assumed to mimic those for the nonequilibrium sequence, Eq. (5.3) holds also for the nonequilibrium sequence. The lhs of Eq. (5.3) is, however, the quantity dU_F which appears in Eqs. (4.2) and (4.4), with the modification that Eqs. (5.2) and (5.3), so far, have focused on one reactive circuit component, whereas Eqs. (4.2) and (4.4) sum over all energy-storing components. Let us now, in this section, limit ourselves to circuits with one degree of freedom. Then Eqs. (4.2) and (5.3) yield

$$T\,dS = dQ - dQ_0\,. \tag{5.4}$$

Eq. (5.4) is our generalization of the familiar $T\,dS = dQ$.

VI. FOKKER-PLANCK APPROXIMATION

The kinetic processes of interest in this paper are usually Markovian processes described by a master equation. In many cases, this can be approximated by a deterministic equation of motion, supplemented by fluctuations which cause small deviations from the deterministic path. In one dimension, we would typically have a probability flux j, generated by a distribution function ρ over some degree of freedom q, given by Eq. (1.6) and repeated here for convenience:

$$j = \rho(q)v(q) - D\frac{\partial\rho}{\partial q}\,. \tag{6.1}$$

Sometimes Eq. (6.1) is written with the diffusion coefficient $D(q)$ under the differentiation sign. The relationship between these two forms has been discussed by the author.[11] Eq. (6.1), or, more properly, the equation derived from it by invoking $\partial\rho/\partial t + \partial j/\partial q = 0$ is called the Fokker-Planck equation. In a series of definitive papers, of which we will here cite only two recent items, van Kampen[15,16] has pointed out that the replacement of the master equation by a Fokker-Planck equation is likely to be unwarranted. There is no question about the validity and relevance of most of van Kampen's discussions and criticisms, and we have cited and invoked van Kampen's viewpoint on a number of occasions in the past. Nevertheless, we hesitate to accept some of van Kampen's stronger statements, such as[16]: "The nonlinear Fokker-Planck equation, which is so often used for describing nonlinear random processes in physics... is an inconsistent approximation, unfit to describe anything beyond the linear noise approximation." Actually van Kampen admits that there are cases in which the "nonlinear" Fokker-Planck equation is valid. ["Nonlinear," here has a rather special meaning: The "linear" case is one in which $v(q)$ in Eq. (6.1) is a linear function of q, and D is independent of q.] In a recent paper,[17] van Kampen applies the Fokker-Planck equation to the case in which a nonlinear mechanical pendulum is subjected to noise by a viscous medium whose stochastic behavior is that characteristic of its equilibrium state and independent of the nonlinear mechanism of the pendulum. The parametric oscillator[18] is a very similar system. In the Appendix we discuss the validity of the Fokker-Planck in further detail. For the moment, we shall simply assume that it is justified.

Let us now assume that we are once again dealing with a slowly shifting steady state. Near such a state, the restoration to this state is

$$v(q) = (q - q_{SS})/\tau\,, \tag{6.2}$$

where q_{SS} represents the steady state. Let us assume that the fluctuations are small enough (i.e., the system large enough) so that we are within the range of validity of Eq. (6.2) and also can take D as constant over the range of interest. Then the steady-state version of Eq. (6.1), $j = 0$, integrates readily to give, as in Sec. I.

$$\rho = C\exp[-(q - q_{SS})^2/2D\tau]\,. \tag{6.3}$$

This, however, is of the same form as an equilibrium distribution biased at q_{SS}. The Boltzmann distribution is of the form $e^{-U/kT}$. If we apply a force which displaces the equilibrium system to q_{SS}, then the energy variation about q_{SS} will be quadratic and of the form

$$\delta U(q) = \tfrac{1}{2}U''(q_{SS})(q - q_{SS})^2\,, \tag{6.4}$$

and therefore the equilibrium distribution will be

$$\rho = C' \exp[-U''(q - q_{SS})^2/2kT] . \quad (6.5)$$

Eqs. (6.3) and (6.5) specify the same distribution if we set $T = U''D\tau/k$. Thus, Eq. (6.3) determines an effective temperature and also, of course, an associated entropy.

As the system becomes larger, and the relative deviation due to fluctuations smaller, the approximation involved in neglecting terms in the exponents of Eqs. (6.3) and (6.5) beyond the quadratic terms improves. This is likely to be obvious, but in case it is not, a detailed discussion can be found in Sec. 5 of Ref. 8.

We might, at this point, be tempted to invoke the equivalence between Eqs. (6.3) and (6.5) as being adequate for the mimicking of equilibrium distributions by nonequilibrium distributions, as invoked in Sec. V. This is, however, too poor an approximation, and we shall go to some trouble at this point, with an equilibrium example, to make this clear. Consider a nonlinear capacitor in which the differential capacitance $C = dq/dV$ increases with increasing charge q. If we take such a capacitor and charge it, but keep it at a constant temperature T, the energy of small fluctuations

$$\langle (q - \langle q \rangle)^2 \rangle / 2C = \tfrac{1}{2}kT \quad (6.6)$$

is independent of the state of charge $\langle q \rangle$. The typical magnitude of the charge fluctuations increases, however, as the capacitor is charged, and as the differential capacitance C is increased. Thus, as the capacitor is charged, $dS > 0$ and $dQ > 0$. Therefore,

$$\langle dU \rangle - \langle V \rangle \langle dq \rangle = dQ > 0 . \quad (6.7)$$

From Eq. (6.5), however, we can easily deduce that

$$\langle U \rangle = U(q_{SS}) + \tfrac{1}{2}kT . \quad (6.8)$$

As the capacitor is charged at constant temperature, Eq. (6.8) yields

$$d\langle U \rangle = dU(q_{SS}) . \quad (6.9)$$

Now if we limit ourselves to Eq. (6.5), without higher-order terms, then the symmetry of the distribution assures us that

$$\langle q \rangle = q_{SS} , \quad d\langle q \rangle = dq_{SS} . \quad (6.10)$$

Furthermore for *any* thermal equilibrium distribution with a single point of maximum probability at q_{SS} it is easy to show, *without* approximation, that

$$\left\langle \frac{dU}{dq} \right\rangle = \left(\frac{dU}{dq} \right)_{q=q_{SS}} , \quad (6.11)$$

or equivalently, for capacitive voltages

$$\langle V \rangle = V(q_{SS}) . \quad (6.12)$$

Putting together Eqs. (6.10) and (6.12) leads us to

$$\langle V \rangle \langle dq \rangle = V(q_{SS})\, dq_{SS} = dU(q_{SS}) . \quad (6.13)$$

Then, using (6.9) and (6.13) in the lhs of (6.7) yields

$$\langle dU \rangle - \langle V \rangle \langle dq \rangle = 0 . \quad (6.14)$$

This, however, is in contradiction to the earlier conclusion, in Eq. (6.7), that $dQ > 0$. Thus, we see that the approximation of Eq. (6.5) is inadequate to account for the ordinary entropy changes found in a nonlinear capacitor when it is charged slowly and traversing a series of thermal-equilibrium states.

Now consider, instead, an asymmetrical distribution, going beyond Eq. (6.5). We then allow for the fact that for a system, as described, where $d^2U/dq^2 = 1/C$ rises with q, the distribution stretches further toward $q > q_{SS}$ than toward $q < q_{SS}$. Thus, $\langle q \rangle > q_{SS}$, in contradiction to Eq. (6.10). Consider now, for clarity, a somewhat special case. Assume that near $q = 0$ the capacitance is constant over a range $|q| < q_1$. Then assume that C increases in the range $q_1 < q < q_2$. Finally, for $q_2 < q$, assume that C is constant again, at its higher value. Thus, as the capacitor is charged, the entropy increase takes place between q_1 and q_2. Now in this range $\langle q \rangle > q_{SS}$, whereas from Eq. (6.12) $\langle V \rangle = V(q_{SS})$. Thus, $\langle V \rangle$ is lower than $V(\langle q \rangle)$, and in computing $\langle V \rangle \langle dq \rangle$ we get a smaller contribution from each range $\langle dq \rangle$ than stated in Eq. (6.13). On the other hand, Eq. (6.8) still holds in the ranges in which the capacitance is constant. Thus, for a value of $q' > q_2$, we have

$$\int_0^{q'} \langle dU \rangle = U(q') - U(0) = \int_0^{q'} V(q)\, dq . \quad (6.15)$$

As just pointed out, however,

$$\langle V \rangle \langle dq \rangle < V(q)\, dq \quad (6.16)$$

as long as $\langle dq \rangle$ and dq represent the same change along the q axis. Thus,

$$\int_0^{q'} \langle dU \rangle - \langle V \rangle \langle dq \rangle > \int_0^{q'} \langle dU \rangle - V(q)\, dq = 0 , \quad (6.17)$$

and this is consistent with our conclusion that $dQ > 0$.

Let us extend these considerations slightly by considering the variation of various terms with the system size, following the kind of consideration already supplied in Sec. 5 of Ref. 8. Let us replace a given circuit by replacing all of its original elements by n identical elements in parallel. The new circuit will then have nonlinearities which appear on the same scale of fields and voltages as in the old circuit, but charges and currents are multiplied by n. (This is, of course, not the only way of going to a larger circuit, and reducing fluctua-

tions.) Then, as pointed out in Ref. 8, the capacitive-charge fluctuations will vary as $\sqrt{n}$ and the voltage fluctuations as $1/\sqrt{n}$. [This also follows from $\frac{1}{2}C(\delta V^2) \sim \frac{1}{2}kT$ and $(\delta Q)^2/2C \sim \frac{1}{2}kT$, and then allowing for the fact that C varies linearly with n.] Now consider the entropy changes caused by taking an uncharged capacitor to some fixed voltage level. While the size of the charge fluctuations varies as $\sqrt{n}$, the ratio of this fluctuation range, for the two charge states under consideration, is independent of n. It is this ratio which determines the entropy change, and ΔS, therefore, is independent of n. This is in contrast to the capacitive energy which varies as n.

If the voltage fluctuations vary as $1/\sqrt{n}$, then the difference between fluctuations to the right and to the left will arise from the asymmetries and will vary as $(1/\sqrt{n})^2$ or $1/n$. It is this sort of asymmetry which determines the difference between $\langle V \rangle$ and other voltages related to the distribution function, such as $V(\langle q \rangle)$. These voltage differences, as can be seen in Eq. (6.17), determine the entropy changes as the capacitor is charged. The voltage differences, of order $1/n$, are multiplied by charge changes (not charge fluctuations) of order n, and thus give a contribution independent of n, which is consistent with the behavior for ΔS discussed above. Therefore, we can see that by going far enough beyond the quadratic approximation of Eq. (6.5) to take into account asymmetry in the distribution function, we do account for the expected entropy changes. Thus, the cubic term in the exponent of the distribution function (i.e., cubic in the deviation from the point of maximum probability) is needed to talk sensibly about entropy changes. Higher-order terms, however, such as $(q - q_{SS})^4$ will go to zero still faster with increasing n, and for large enough n can be neglected.

VII. ASYMMETRY IN THE DISTRIBUTION FUNCTION

We have seen, in Sec. VI, that the lowest-order terms, giving a deviation from a symmetric distribution function, are needed for a sensible discussion of entropy changes. It is clear, on the other hand, that if we keep many higher-order moments in our distribution functions there will be no reason for the steady-state solution of Eq. (6.1),

$$\rho = C \exp \int \frac{v}{D}\, dq \ , \tag{7.1}$$

to resemble $\exp(-U/kT_N)$. After all, v/D reflects the details of the behavior of the dissipative circuit elements, whereas U represents the physics of a nonlinear reactance, say, a capacitor. We can choose T_N to match the behavior in the quadratic terms in the exponents, but that will not help for the higher-order terms. Let us, in this section, concentrate on the case where only the lowest-order terms in asymmetry, discussed in Sec. VI, have to be invoked. We continue to focus on a circuit with only one reactance. This present section is, essentially, a slight rewording of Sec. 6 of Ref. 8. (The discussion in Ref. 8 is basically correct, but the explanation is poor in the later parts of that section.)

Let us first introduce an auxiliary quantity Δ, as follows

$$U(q) = U(q_0) + U'(q_0)(q - q_0) + \Delta \ . \tag{7.2}$$

Thus, Δ represents the variation in energy, including quadratic and higher terms, about a point q_0 which we will take to be the point of maximum probability for the distribution function. Eq. (4.2) can be written in the form, using Q_F of Eq. (2.5),

$$dQ_F = dQ - dQ_0 = dU_F = \langle dU \rangle - \left\langle \frac{dU}{dq} \right\rangle \langle dq \rangle \ . \tag{7.3}$$

With the use of Eq. (7.2), this becomes

$$dQ_F = \langle dU \rangle - U'(q_0)\langle dq \rangle - \left\langle \frac{d\Delta}{dq} \right\rangle \langle dq \rangle \ . \tag{7.4}$$

Now let us invoke a distribution function, for the nonequilibrium circuit, of the form

$$\rho = C \exp(-\Delta/kT_N) \exp[-\beta(\Delta/kT_N)^{3/2}] \ . \tag{7.5}$$

Without the final right-hand exponential factor, this would just be a thermal equilibrium distribution, in the presence of a force (voltage, in the case of a capacitor) biasing the reactive device at $q = q_0$. The final factor, involving the coefficient β, permits the asymmetry of the distribution function in Eq. (7.1) to be different from that of thermal equilibrium. Instead of $(\Delta/kT_N)^{3/2}$ we could have used $(q - q_0)^3$. We shall, hereafter, only account for effects which are first order in β, and in the other asymmetry parameters, e.g., the third derivative of Δ with respect to q. Thus, cross effects between β and Δ^m will be ignored.

We will want to compare Eq. (7.4) to

$$T_N\, dS = kT_N \int \delta\rho \ln\rho \, dq \ , \tag{7.6}$$

where $\delta\rho$ represents the change between two different distributions of the form (7.5). Using (7.5) in (7.6) gives

$$T_N\, dS = -kT_N \int \delta\rho \left[-\frac{\Delta}{KT_N} - \beta \left(\frac{\Delta}{kT_N} \right)^{3/2} \right] dq \ . \tag{7.7}$$

Replacing Δ in Eq. (7.7) through the use of Eq. (7.2) yields

$$T_N\,dS = \langle \delta U\rangle - U'(q_0)\langle dq\rangle + \beta k T_N \int \delta\rho\left(\frac{\Delta}{kT_N}\right)^{3/2} dq\,. \tag{7.8}$$

In thermal equilibrium $\beta = 0$, and the final rhs terms of both Eqs. (7.4) and (7.8) vanish, and $T_N\,dS = dQ_F$. We want to recognize, however, that in the dissipative steady state, as the system becomes large, β becomes small, but is nonvanishing.

Consider first the $\langle d\Delta/dq\rangle$ term in Eq. (7.4):

$$\left\langle \frac{d\Delta}{dq}\right\rangle = \frac{\int (d\Delta/dq) e^{-\Delta/kT_N} \exp^{-\beta(\Delta/kT_N)^{3/2}} dq}{\int e^{-\Delta/kT_N} \exp^{-\beta(\Delta/kT_N)^{3/2}} dq}\,. \tag{7.9}$$

To zeroth order in β, we can take the normalization integral in the rhs denominator simply as $Z = \int e^{-\Delta/kT_N}\,dq$. In the rhs numerator of Eq. (7.9), we take

$$\exp[-\beta(\Delta/kT_N)^{3/2}] = 1 - \beta(\Delta/kT_N)^{3/2}\,. \tag{7.10}$$

Only the β term from (7.10) contributes to the integral in the numerator of Eq. (7.9), leaving

$$\left\langle \frac{d\Delta}{dq}\right\rangle = -\frac{\beta}{Z}\int \left(\frac{d\Delta}{dq}\right)\left(\frac{\Delta}{kT_N}\right)^{3/2} e^{\Delta/kT_N}\,dq = -\frac{\beta k T_N}{Z} 2\int_0^\infty e^{-x} x^{3/2}\,dx\,. \tag{7.11}$$

The definite integral in Eq. (7.11) is a gamma function, and therefore the final rhs term of Eq. (7.4) becomes

$$-\left\langle \frac{d\Delta}{dq}\right\rangle \langle dq\rangle = (\beta k T_N/Z) 2\Gamma\left(\tfrac{5}{2}\right) \int \delta\rho q\,dq\,. \tag{7.12}$$

Consider now the other term involved in our comparison, the last rhs term of Eq. (7.8),

$$\beta k T_N \int \delta\rho(\Delta/kT_N)^{3/2}\,dq\,. \tag{7.13}$$

Since this expression already contains a factor β, we can neglect any further asymmetry in $\delta\rho$ and in Δ. We can thus assume that $\delta\rho$, as used in (7.13), represents a change from one equilibrium distribution function to another. Such a change has two possible sources. One is a displacement of the point q_0 to which the distribution function is biased. The other is a change in temperature. A change in temperature gives a change in the spread of the distribution function. $\delta\rho$ as a function of $q - q_0$ will then be an even, or quadratic, function, to lowest order in $q - q_0$. This will be multiplied by $\Delta^{3/2}$ which, neglecting asymmetry, is proportional to $(q - q_0)^3$, and odd about q_0. Thus, we are left with a vanishing contribution to the integral in (7.13). Consider now the alternative source for $\delta\rho$, the displacement of q_0. To the lowest order in the asymmetry, this will be indistinguishable from a rigid displacement of the existing distribution function. A displacement of the distribution by dq_0 gives

$$\delta\rho = -dq_0 \frac{\partial\rho}{\partial q} = dq_0 \frac{1}{kT_N Z} e^{-\Delta/kT_N} \frac{d\Delta}{dq}\,. \tag{7.14}$$

If this is substituted into (7.13), we find

$$\beta\,dq_0\,\frac{1}{Z}\int_{-\infty}^{\infty} e^{\Delta/kT_N}\left(\frac{\Delta}{kT_N}\right)^{3/2}\left(\frac{d\Delta}{dq}\right) dq = \beta k T_N Z^{-1} 2\Gamma\left(\tfrac{5}{2}\right) dq_0\,, \tag{7.15}$$

which is equivalent to Eq. (7.12).

Thus, for distributions which are narrow enough to warrant the approximations of this section, we still find $T_N\,dS = dQ_F$, despite the fact that we allowed, through the use of β, a disparity between the thermal-equilibrium distribution functions and those of the nonequilibrium circuit.

VIII. SEVERAL DEGREES OF FREEDOM

An earlier paper[9] examined the circuit with several reactances in some detail, and we will not duplicate that discussion here. That analysis discussed the conditions under which such a circuit leads to detailed balance. Detailed balance was invoked since it is obeyed in equilibrium, and if we are going to simulate equilibrium, then we can expect detailed balance. That, however, is really too restrictive a demand. To find a relationship between dU_F and $T\,dS$ we only need to mimic equilibrium distribution functions, and not necessarily the kinetics leading to them. Thus, the earlier analysis[9] while correct, is too demanding, and thus too pessimistic in its conclusions. Even this earlier analysis, however, made it clear that there are *some* circuits far from equilibrium, with more than one degree of freedom, which permit us to replace dU_F in Eq. (4.4), or alternatively in the differential version of Eq. (2.5),

$$dU_F = d\,Q_F\,, \tag{8.1}$$

by $\sum T_i\,dS_i$. In this expression each reactance is presumed to exhibit narrow fluctuations defining a separate temperature for that reactance.

Let us assume that a circuit contains a set of reactances exhibiting narrow fluctuations. As the circuit is subject to slow changes, each reactance will be taken through a series of distribution functions, each mimicking an equilibrium distribution function. Now the total value of dU_F can be separated into a series of contributions, one per reactance:

$$dU_F = \sum_i dU_{F_i}\,. \tag{8.2}$$

Furthermore, for each reactance we must have

$$dU_{F_i} = T_i\, dS_i \tag{8.3}$$

and thus

$$dU_F = \sum T_i dS_i\,. \tag{8.4}$$

Note that $\sum S_i$ need not be the entropy of either the equilibrium or the nonequilibrium system. That would require that the fluctuations in the different degrees of freedom be uncorrelated.

OVERVIEW: SECTIONS 2-8

We have pointed out that there is a generalization of $T\,dS = dQ$, applicable to some open dissipative systems which are very far from equilibrium. While the relationship, in this exact form, is subject to a number of limitations discussed in detail in the preceding sections, we want to stress that Eq. (4.4)

$$dQ = dU_F + dQ_{SS} + \delta L$$

is much more general. As pointed out in Sec. IV, the steady-state heat dissipation dQ_{SS} is the only unrecoverable form of heat exchange in this expression. dU_F and δL change sign if we reverse the modulation of the system. We also once again stress that the generalization of $T\,dS = dQ$ does invoke the fact that S is the actual entropy in the presence of the ongoing process, defined via $S = -k\int \rho \ln\rho\, dq$.

APPENDIX

Consider a system in which $\rho(q)$ varies slowly compared to the geometrical scale of the basic stochastically independent physical-displacement event in q space. For particles moving along a real physical q axis, this elementary displacement event would be a mean free path. Figure 5 shows two distributions which are tangent at $q = q_m$, and close to each other over a range $q_1 < q < q_2$. Let us assume, as indicated, that $|q_2 - q_1|$ is large compared to the elementary displacement event. Then

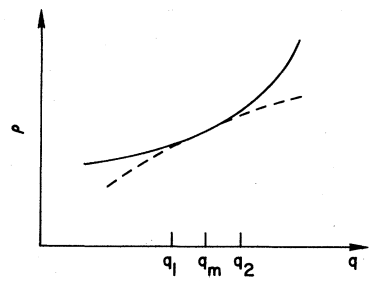

FIG. 5. Two different distribution functions tangent at $q = q_m$.

the probability flux at $q = q_m$ must be the same for the two distribution functions shown in Fig. 5. If it were otherwise, it would mean that the behavior near $q = q_m$ depends on the earlier history, reflecting the behavior outside the range $q_1 < q < q_2$. But that would not be a Markovian process. If the two distributions give the same the flux at $q = q_m$, that flux must be independent of the higher derivatives $\partial^2\rho/\partial q^2$, $\partial^3\rho/\partial q^3$, etc. This, in turn, means that the flux is a linear function of ρ and $\partial\rho/\partial q$, as assumed in Eq. (6.1).

We can restate the above point in a more formal way. Again, we shall focus on the case where the jumps in q space occur over small distances compared to those over which $\rho(q)$ varies appreciably. One example would be a spatially nonuniform transistor structure with a mean free path small compared to the scale of the structure. An alternative example would be chemical diffusion of an interstitial defect in a macroscopically inhomogeneous crystal. Let the size of successive jumps made in q space be denoted by δq_i, and let us, for clarity, restrict this discussion to a one-dimensional space. The values of δq_i will be specified by a probability distribution $w_i(\delta q_i)$. Consider the sum of N successive displacements

$$S = \sum_{i=1}^{N} \delta q_i\,, \tag{A1}$$

with N large enough that the probability distribution for S is determined by the central-limit theorem, but with N small enough that S is small compared to the geometrical scale of the problem and all the $w_i = w$ we are essentially alike. The probability distribution $\Omega(S)$ for S must then be of the form

$$\Omega(S) = \exp[-\alpha(S - S_0)^2]\,. \tag{A2}$$

The net displacement S_0 must clearly arise from the lack of symmetry in the jump probability w, and thus

$$S_0 = N\int_{-\infty}^{\infty} w(\delta q)\delta q\, d\delta q\,. \tag{A3}$$

$1/\alpha$ is a measure of the mean-square deviation in displacement, and would clearly be the same if $w(\delta q)$ were shifted in δq space to make the integral in Eq. (A3) vanish. In that case, however,

$$\langle S^2\rangle = \left\langle \left(\sum_{i=1}^{N} \delta q_i\right)^2 \right\rangle = \sum_{i=1}^{N} \langle \delta q_i{}^2\rangle = N\langle \delta q^2\rangle \tag{A4}$$

since $\langle \delta q_i \delta q_j\rangle$ vanishes if $i \neq j$. Thus the mean-square deviation in S is proportional to N, and α in Eq. (A2) must be proportional to $1/N$. Both $\langle S\rangle$ and $\langle (S - S_0)^2\rangle$ are then proportional to N. It is then easy to show from the distribution for $\Omega(S)$ given by Eq. (A2) that the higher moments $\langle S^n\rangle$ for $n > 2$

must then go to zero faster than N.

Up to this point we have considered N successive "jumps" without asking whether this corresponds to a fixed time interval or not. Let us, therefore, define our "jump" more carefully by requiring $w(\delta q)$ to represent the displacement that occurs in a given short time interval, which need not necessarily be the time in which the system—on the average—has made a jump. $w(\delta q)$ may thus contain a substantial δ function representing the probability that the particle has not moved. Then the N jumps do represent a fixed elapsed time. The condition, however, that the higher-order moments $\langle\langle S^n \rangle\rangle$, for $n > 2$) go to zero faster than the elapsed time is the usual condition for the applicability of the Fokker-Planck equation.[19]

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