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Thermodynamic and stochastic theory of electrical circuits

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We begin the development of a thermodynamic and stochastic theory of electrical circuits approaching nonequilibrium stationary states containing linear or nonlinear capacitors, resistors, and inductors. We restrict ourselves to circuits with only point attractors. The theory centers around a function ϕ, and we show that (1) it is the macroscopic driving force to a stationary state, (2) it is a global Liapunov function, (3) it provides necessary and sufficient conditions for the existence and stability of stationary states, (4) its time derivative is a component of the total dissipation, (5) it is an excess work of moving the circuit away from the stationary state, and (6) it determines a stationary probability distribution of a Fokker-Planck equation. The generalization from linear to nonlinear circuits is made with the concept of an instantaneous mapping from the nonlinear circuit to a thermodynamically and kinetically equivalent linear circuit. A translation of chemical to electrical networks holds at the thermodynamic but not stochastic level of description.

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I. INTRODUCTION

In a series of articles [1–4] Ross, Hunt, and Hunt (RHH) have developed a thermodynamic and stochastic description of kinetic chemical systems valid both near and far from equilibrium, including the relaxation to stationary states and conditions of stability for such states. Their theory so far encompasses both linear and nonlinear one- and multidimensional systems that evolve in time to a limit point (stable nodes or foci, but not stable oscillations, for example). The theory has been extended by Ross, Chu, Hjelmfelt, and Velarde [5] to the transport processes of linear and nonlinear diffusion, thermal conduction, and viscous flow. Here we further extend the RHH theory to electrical networks.

There exists extensive prior work in the general field of the title of this article [6–21]. Landauer has discussed the relevance of a number of theorems of Prigogine's group [6–8] and Nicolis [9] to electrical circuits [10, 11]. Stability analysis of electrical circuits has a long tradition and is discussed in numerous texts [12–14]. Likewise, the role of fluctuations in electrical circuits has received much attention [10, 11, 15–19], in part due to the importance of bistable memory elements.

We begin with a description of the RHH [1–4] approach and use a chemical system as a basis for a brief review. Consider a one-dimensional chemical reaction [1, 21] system shown in Fig. 1,

$$\begin{aligned} &A+(r-1)X \overset{k_1,k_{-1}}{\rightleftharpoons} rX, \\ &X \overset{k_2,k_{-2}}{\rightleftharpoons} B, \end{aligned} \tag{1}$$

where A and B are held constant in time. The time evolution of the intermediate X is given by

$$\frac{dX}{dt} = k_1AX^{r-1} - k_{-1}X^r - k_2X + k_{-2}B. \tag{2}$$

In a linear system ($r = 1$) the stationary solution of Eq. (2) is given by

$$X^s = \frac{k_1A + k_{-2}B}{k_{-1} + k_2} \tag{3}$$

and thus

$$\frac{dX}{dt} = -(X - X^s)(k_{-1} + k_2). \tag{4}$$

The generalization of Eq. (4) to nonlinear systems ($r \neq 1$) is through the concept of instantaneous thermodynamic and kinetic equivalence (ITKE). At each value of the variable X, or correspondingly at each instant in time, it is possible to identify a linear reaction mechanism where the constraints (temperature, concentrations of A and B, etc.), the equilibrium constants, and the microscopic forward and reverse rates of the ITKE linear system are identical to those of the nonlinear system. For ($r \neq 1$) in Eq. (1) the ITKE system (where $r = 1$) is given by

$$\begin{aligned} &k_1' = k_1X^{r-1}, \quad k_2' = k_2, \\ &k_{-1}' = k_{-1}X^{r-1}, \quad k_{-2}' = k_{-2}, \end{aligned} \tag{5}$$

where the (′) quantities indicate those of the ITKE system. The stationary states of the ITKE system are given by

$$X^* = X'^s = \frac{k_1'A + k_{-1}'B}{k_{-1}' + k_2'} = \frac{k_1AX^{r-1} + k_{-2}B}{k_{-1}X^{r-1} + k_2}. \tag{6}$$

ITKE guarantees that the time derivatives of X in both the nonlinear and linear ITKE system are identical,

$$\frac{dX}{dt} = -(X - X^*)(k_{-1}' + k_2'). \tag{7}$$

In the following we use a (*) to denote the reference concentration of the system; for linear systems it is just the stationary-state concentration, or for nonlinear systems it is the stationary-state concentration of the corresponding ITKE system.

For a given conversion of dn_A moles of A, dn_B moles of B, and dn_X moles of X, the change in the free energy of the system as shown in Fig. 1 is

$$\begin{aligned} dM &= dG_1 + dA_2 + dG_3 \\ &= \mu_A dn_A + \mu_X dn_X + \mu_B dn_B, \end{aligned} \tag{8}$$

where dG_1 and dG_3 are differential changes in the Gibbs free energy for the compartments 1 and 3 in Fig. 1, each held at constant temperature and pressure (specific to 1 or 3), and dA_2 is the differential change in the Helmholtz free energy for compartment 2 held at the same constant temperature and constant volume. If an identical conversion were to occur but at the reference concentration, then we have

$$dM^* = \mu_A dn_A + \mu_X^* dn_X + \mu_B dn_B \tag{9}$$

and the difference defines $d\phi$,

$$d\phi = dM - dM^* = (\mu_X - \mu_X^*) dn_X, \tag{10}$$

which is the central function in the theory.

RHH [1–3] examined the properties of ϕ and showed the following.

(i) ϕ is the affinity of a chemical species and is the macroscopic driving force towards the stationary states.

(ii) ϕ is a global Liapunov function. The function ϕ is greater than or equal to zero, bounded, and its time derivative is negative except at the stationary state where it is zero. ϕ is a minimum in stable stationary states and a maximum in unstable stationary states.

(iii) ϕ provides global necessary and sufficient conditions for the existence of stationary states ($\delta\phi \,|_s \geq 0$ or $\partial\phi/\partial X \,|_s = 0$) and their stability ($\partial^2\phi/\partial X^2 \,|_s > 0$ for stable stationary states, < 0 for unstable stationary states, and $\partial^3\phi/\partial X^3 \,|_s = 0$ for critical stationary states).

(iv) ϕ is a component of the total dissipation. $D = (\mu_A - \mu_X^*)\dot{A} + (\mu_X^* - \mu_B)\dot{B} - \dot{\phi}$. The part of the dissipation not represented by $\dot{\phi}$ is due to the conversion of A to X at the pressure X^* but at the rate $\dot{A}$ and the conversion of X at the pressure X^* to B at the rate $\dot{B}$; ϕ represents the dissipation due to the displacement of X from X^*.

(v) $-d\phi$ is the excess work provided by a spontaneous infinitesimal change in the system beyond that required to cause an equivalent opposite change in the (*) system.

(vi) ϕ gives the stationary probability distribution of the stochastic master equation describing Eq. (1), $P^s(X) \propto \exp(-\phi/RT)$. This is an extension of Einstein's fluctuation formula to nonequilibrium systems.

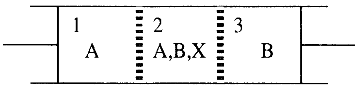

FIG. 1. A chemical reaction apparatus with three volumes divided by selective membranes. The membrane between 1 and 2 is permeable only to A, and the membrane between 2 and 3 is permeable only to B. Pistons insure that the pressure of A in volumes 1 and 2 and the pressure of B in volumes 2 and 3 remain constant in time. A catalyst is in volume 2, which ensures that the reaction occurs only in volume 2.

For multidimensional systems RHH [2, 4] consider reaction mechanisms of the type

$$\begin{aligned} &A + (r_1 - 1)X_1 \rightleftharpoons r_1 X_1, \\ &s_1 X_1 + (r_2 - 1)X_2 \rightleftharpoons (s_1 - 1)X_1 + r_2 X_2, \\ &s_N X_N \rightleftharpoons (s_N - 1)X_N + B. \end{aligned} \tag{11}$$

The multidimensional generalization of Eq. (10) becomes

$$d\phi = \sum_i (\mu_{Xi} - \mu_{Xi}^*) dX_i. \tag{12}$$

For linear systems with arbitrary stationary states and for nonlinear systems with a stationary state of equilibrium, ϕ is a state function and properties (i)–(v) hold. However, for nonlinear systems with arbitrary stationary states, Eq. (12) is an inexact differential. Properties (i)–(v) follow since they depend on $d\phi$, however property (vi) depends on ϕ. Therefore, to integrate Eq. (12), a path of integration must be supplied. RHH have shown that if the path of integration is the deterministic path, then property (vi) follows.

In the development of the thermodynamic theory for linear and nonlinear heat conduction, diffusion, and viscous flow [5], properties (i)–(v) are shown to hold. Given the excess work ϕ, a stochastic equation is sought for which $\exp(-\phi/RT)$ is a stationary solution. For viscous flow this is a Fokker-Planck equation with state-independent noise for linear systems, and state-dependent noise for nonlinear systems. For linear and nonlinear thermal conduction it is a Fokker-Planck equation with state-dependent noise, and for diffusion it is a master equation.

In this manuscript we present a thermodynamic and stochastic theory of some representative resistance-capacitance (RC), resistance-inductance (LR), and resistance-inductance-capacitance (LRC) circuits analogous to the development for chemical reactions and the transport of mass and heat.

The concept of instantaneous thermodynamic and kinetic equivalence is known and used in electrical circuit theory and we begin with that topic.

II. INSTANTANEOUS THERMODYNAMIC AND KINETIC EQUIVALENCE

The RHH theory of nonlinear chemical systems depends on the concept of instantaneous thermodynamic and kinetic equivalent (ITKE) [1] reaction mechanisms or equivalent networks. Two chemical systems are ITKE if the constraints, the equilibrium constants, and the microscopic rates of each corresponding step are identical. Thus for ($r \neq 1$) in Eq. (1) there exists at each value of the variable X, or at each instant in time, a unique mapping to an ITKE system with ($r = 1$). At this value of X the rate of formation of X from A, X from B, the rate of dissipation, and all other instantaneous kinetic and ther-

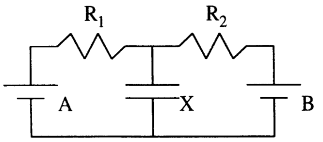

FIG. 2. One-dimensional *RC* circuit; the resistances and capacitances are independent of voltage for Sec. III A and dependent on voltages for Sec. III C.

modynamic properties are identical in the nonlinear and the ITKE linear reaction mechanism.

This concept of ITKE translates to electrical circuits. Two electrical circuits are ITKE if the rates of change of the voltages, the currents, and the rates of dissipation are identical. In Fig. 2 we show an electrical circuit which we assume to be nonlinear. The time evolution of the voltage is given by

$$\frac{dV_X}{dt} = \frac{V_A - V_X}{C(V_X)R_1(V_A, V_X)} - \frac{V_X - V_B}{C(V_X)R_2(V_X, V_B)}, \tag{13}$$

and the resistances are functions of the indicated voltages. For each value of the state variable we define an ITKE linear system which we denote with a ($'$). The time evolution of the voltage in this system is given by

$$\frac{dV_X'}{dt} = \frac{V_A' - V_X'}{C'R_1'} - \frac{V_X' - V_B'}{C'R_2'}. \tag{14}$$

If we set $V_A = V_A'$, $V_B = V_B'$, and $V_X = V_X'$, then the two systems have identical thermodynamic properties including the maximum work which can be extracted by moving charges among A, X, and B. If we add the additional requirements that $R_1' = R_1(V_A, V_X)$, $R_2' = R_2(V_X, V_B)$, and $C = C'$, then the rate of change of V_X (or V_X'), the currents through R_1 and R_1', the currents through R_2 and R_2', and the dissipation are identical. By measuring voltages, currents, rates of dissipation, and all other instantaneous quantities, these two circuits are indistinguishable at that instant. For each value of V_X there is a different ($'$) system, and as the system evolves in time we define a new ITKE circuit at each instant.

The concept of equivalent networks is known and used in circuit theory. "Two n-terminal resistive black boxes N_1 and N_2 are equivalent if they can be interchangeably connected to the same ***arbitrary*** n-terminal network N without affecting the values of the voltages and currents inside N [12]." A more restricted specialization of this statement is that two black boxes N_1 and N_2 are equivalent at a particular operating point of a network N if either may be connected to N without affecting the values of the voltages and currents inside N at that operating point [12]. Systems which show ITKE satisfy this condition, since the voltage drop across and all the currents in two ITKE systems are identical. Thus, at each instant one may replace the other in a larger circuit N.

III. ELECTRICAL NETWORKS FAR FROM EQUILIBRIUM

Throughout this section we assume all resistances, capacitances, and inductances are positive although their differentials need not be. We also assume that the circuit is isothermal.

A. Linear one-dimensional *RC* networks

We formulate the thermodynamics of electrical processes far from equilibrium using the methods developed for chemical and transport processes. We first consider a one-dimensional linear electrical system, and then generalize to multidimensional and nonlinear systems. Figure 2 shows a typical linear electrical circuit if we take the resistances and capacitances to be independent of the voltages. The time dependence of the voltage across the capacitor labeled X is given by

$$\begin{aligned} \frac{dV_X}{dt} &= \frac{V_A - V_X}{C_X R_1} - \frac{V_X - V_B}{C_X R_2} \\ &= -\frac{V_X - V_X^s}{C_X}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = f(V_X), \end{aligned} \tag{15}$$

where the stationary-state voltage V_X^s is

$$V_X^s = \left(\frac{V_A}{R_1} + \frac{V_B}{R_2}\right)\left(\frac{1}{R_1} + \frac{1}{R_2}\right)^{-1}. \tag{16}$$

For a given transfer of charge among V_A, V_X, and V_B, the change in the energy of the system is

$$dE = V_A dn_A + V_X dn_X + V_B dn_B, \tag{17}$$

where dn_i denotes the transfer of charge at V_i. For an identical transfer of charge but at the stationary state we have

$$dE^s = V_A dn_A + V_X^s dn_X + V_B dn_B. \tag{18}$$

The difference between Eqs. (17) and (18) defines the differential $d\phi$ which is an excess work.

$$d\phi = (V_X - V_X^s)dn_X = (V_X - V_X^s)C_X dV_X. \tag{19}$$

Integration of Eq. (19) yields ϕ,

$$\begin{aligned} \phi &= -\left(\frac{1}{R_1} + \frac{1}{R_2}\right) C_X^2 \int f(V_X) dV_X \\ &= \frac{C_X}{2}(V_X - V_X^s)^2. \end{aligned} \tag{20}$$

ϕ is greater than zero except at a stationary state, where it is zero, and it is bounded.

The time derivative of ϕ,

$$\frac{d\phi}{dt} = (V_X - V_X^s)C_X \frac{dV_X}{dt} = -(V_X - V_X^s)^2 \left(\frac{1}{R_1} + \frac{1}{R_2}\right), \tag{21}$$

is always negative except at the stationary state, where it is zero. Thus ϕ decreases to a minimum as the circuit evolves from an arbitrary state to a stationary state; it is a Liapunov function and expresses the macroscopic driving force towards the stationary state. ϕ also gives necessary and sufficient stability properties of the stationary state,

$$\left.\frac{\partial\phi}{\partial V_X}\right|_s = C_X(V_X - V_X^s)\,|_s = 0,$$
$$\frac{\partial^2\phi}{\partial V_X^2} = C_X > 0, \tag{22}$$

and hence ϕ is a minimum in the stationary state and the stationary state is stable. Another way of stating the stability condition of the stationary state is

$$\delta\phi\,|_s \geq 0; \tag{23}$$

if for every variation at the stationary state Eq. (23) is satisfied, then excess work is necessary and the stationary state is stable. This is the analog for stationary states of the criteria of equilibrium formulated by Gibbs [22].

Power is dissipated by the resistors R_1 and R_2, and the heat generated by dissipation is

$$D = \frac{(V_A - V_X)^2}{R_1} + \frac{(V_X - V_B)^2}{R_2}. \tag{24}$$

The total dissipation can be rewritten as

$$D = D^s - \dot{\phi}, \tag{25}$$

and thus $\dot{\phi}$ is a component of the total dissipation. Equation (25) indicates that the dissipation in the stationary state is a minimum in agreement with the well-known theorem of Prigogine [6], which holds for this strictly linear system [23, 24].

For a chemical system ϕ is the stationary solution of a stochastic birth-death master equation, $P(V_X) = \exp(-\phi/RT)$, in the thermodynamic limit of a large number of particles. We seek a stochastic equation with a stationary solution given by the exponential of $-\phi$ for an electrical circuit. We write Eq. (15) as a Langevin equation [25, 26]

$$\frac{dV_X}{dt} = \frac{V_A - V_X}{C_X R_1} - \frac{V_X - V_B}{C_X R_2} + \sqrt{2\Gamma}\epsilon = f(V_X) + \sqrt{2\Gamma}\epsilon, \tag{26}$$

where ϵ is uncorrelated noise. This Langevin equation can be converted into a Fokker-Planck equation

$$\frac{\partial P(V_X,t)}{\partial t} = -\frac{\partial f(V_X)P(V_X,t)}{\partial V_X} + \frac{\partial^2 \Gamma P(V_X,t)}{\partial V_X^2}. \tag{27}$$

If we assume that the exponential of ϕ for an electrical network gives the stationary solution just as in a chemical system, then the stationary solution and the amplitude of the noise are

$$\Gamma = \left(\frac{1}{R_1} + \frac{1}{R_2}\right)\frac{kT}{C_X^2},$$
$$P(V_X) \propto \exp[-C_X(V_X - V_X^s)^2/2kT] = \exp(-\phi/kT), \tag{28}$$

where k is Boltzmann's constant and T is the thermodynamic temperature. For this linear circuit, the amplitude of the noise (Γ) is independent of the state variable V_X.

This probability distribution is consistent with fluctuations given by equilibrium statistical thermodynamics. From the theory of the grand-canonical ensemble, fluctuations in numbers of particles in an open system is Gaussian [27],

$$P(n_X) \propto \exp\left(-\frac{(n_X - < n_X >)^2}{2kT(\partial < n_X > /\partial V_X)}\right), \tag{29}$$

where n_X is the number of charges on the capacitor, and $< n_X >$ denotes the average which is the macroscopic observable. The number of charges is related to the voltage by the capacitance, $C_X V_X = n_X$, so

$$P(V_X) \propto \exp\left(-\frac{C_X(V_X - < V_X >)^2}{2kT}\right). \tag{30}$$

The equilibrium condition requires $V_A = V_B =< V_X >$, and this is identical to Eq. (28), where the stationary state V_X^s is equilibrium. Thus, the probability distribution obtained from the RHH theory at equilibrium is consistent with that obtained from equilibrium statistical mechanics.

B. Linear N-dimensional RC networks

The results of the preceding section generalize to multidimensional systems of the type shown in Fig. 3. The time dependence of the voltage on a capacitor is

$$\begin{aligned}\frac{dV_i}{dt} &= \frac{V_{i-1} - V_i}{C_i R_i} - \frac{V_i - V_{i+1}}{C_i R_{i+1}} \\ &= -\frac{V_i - V_i^s}{C_i}\left(\frac{1}{R_i} + \frac{1}{R_{i+1}}\right) \\ &\quad + \frac{V_{i-1} - V_{i-1}^s}{C_i R_i} + \frac{V_{i+1} - V_{i+1}^s}{C_i R_{i+1}},\end{aligned} \tag{31}$$

where $1 \leq i \leq N$ and the stationary-state voltages are given by

$$V_i^s = \left(\frac{V_{i-1}^s}{R_i} + \frac{V_{i+1}^s}{R_{i+1}}\right)\left(\frac{1}{R_i} + \frac{1}{R_{i+1}}\right)^{-1}. \tag{32}$$

For a given transfer of charge, the change in the energy of the system is

$$dE = \sum_{i=0}^{N+1} V_i dn_i, \tag{33}$$

where dn_i denotes the transfer of charge at V_i. For an identical transfer of charge, but at the stationary-state voltages, we have

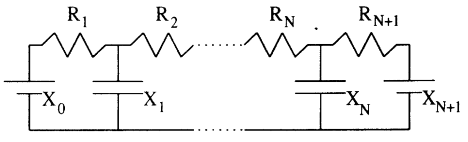

FIG. 3. Multidimensional RC circuit; the resistances and capacitances are independent of voltage for Sec. III B and dependent on the voltages for Sec. III D.

$$dE^s = \sum_{i=0}^{N+1} V_i^s dn_i, \tag{34}$$

and the difference defines the differential $d\phi$ of the excess work,

$$d\phi = \sum_{i=1}^{N}(V_i - V_i^s)dn_i = \sum_{i=1}^{N}(V_i - V_i^s)C_i dV_i. \tag{35}$$

Integration results in

$$\phi = \sum_{i=1}^{N}\frac{C_i}{2}(V_i - V_i^s)^2. \tag{36}$$

As in the one-dimensional case, ϕ is greater than zero in arbitrary states and equal to zero in stationary states. The time evolution of ϕ is given by

$$\begin{aligned}\frac{d\phi}{dt} &= \sum_{i=1}^{N}(V_i - V_i^s)C_i\frac{dV_i}{dt} = \sum_{i=1}^{N}(V_i - V_i^s)\left(\frac{V_{i-1} - V_i}{R_i} - \frac{V_i - V_{i+1}}{R_{i+1}}\right)\\ &= \sum_{i=1}^{N}(V_i - V_i^s)\left(\frac{V_{i-1} - V_{i-1}^s + V_i^s - V_i}{R_i} - \frac{V_i - V_i^s + V_{i+1}^s - V_{i+1}}{R_{i+1}}\right)\\ &= \sum_{i=1}^{N+1}\frac{1}{R_i}[-(V_i - V_i^s)^2 + 2(V_i - V_i^s)(V_{i-1} - V_{i-1}^s) - (V_{i-1} - V_{i-1}^s)^2]\\ &= \sum_{i=1}^{N+1}\frac{-1}{R_i}[(V_i - V_i^s) - (V_{i-1} - V_{i-1}^s)]^2,\end{aligned} \tag{37}$$

which is negative in arbitrary states and zero in stationary states. ϕ also gives necessary and sufficient stability properties

$$\left.\frac{\partial\phi}{\partial V_i}\right|_s = C_i(V_i - V_i^s)\,|_s = 0,$$
$$\frac{\partial^2\phi}{\partial V_i^2} = C_i > 0, \quad \frac{\partial^2\phi}{\partial V_i V_j} = 0, \tag{38}$$

and thus ϕ is a minimum in the stationary state and V^s is stable. Hence Eq. (23) holds. ϕ is a Liapunov function which yields the evolution of the system.

The power dissipated by the resistors is given by

$$D = \sum_{i=1}^{N+1}\frac{(V_i - V_{i-1})^2}{R_i} \tag{39}$$

and can be rewritten as

$$D = D^s - \dot{\phi}. \tag{40}$$

Hence $\dot{\phi}$ is a component of the total dissipation. Again, we see that the dissipation in the stationary state is a minimum in agreement with the minimum entropy production theorem of Prigogine for this strictly linear system.

We seek the stochastic equation for which the stationary probability distribution is given by $\exp(-\phi/kT)$. If we write Eq. (31) as a Langevin equation, then

$$\frac{dV_i}{dt} = \frac{V_{i-1} - V_i}{C_i R_i} - \frac{V_i - V_{i+1}}{C_i R_{i+1}} + \sqrt{2\Gamma_i}\epsilon_i = f_i + \sqrt{2\Gamma_i}\epsilon_i. \tag{41}$$

The Fokker-Planck equation which corresponds to this Langevin equation is

$$\frac{\partial P(V_i,t)}{\partial t} = -\sum_i\frac{\partial f_i P}{\partial V_i} + \sum_{i,j}\Gamma_{i,j}\frac{\partial^2 P}{\partial V_i \partial V_j}. \tag{42}$$

If we require the stationary-state probability distribution to have the form

$$P \propto \exp\left(\sum_i\frac{C_i}{2kT}(V_i - V_i^s)^2\right) = \exp(-\phi/kT), \tag{43}$$

then the amplitude of the noise must be

$$\begin{aligned}\Gamma_{ii} &= \left(\frac{1}{R_i} + \frac{1}{R_{i+1}}\right)\frac{kT}{C_i^2}, \quad i = 1,\ldots,N\\ \Gamma_{i,i-1} &= \frac{-kT}{C_i C_{i-1} R_i}, \quad i = 2,\ldots,N\\ \Gamma_{i,i+1} &= \frac{-kT}{C_i C_{i+1} R_{i+1}}, \quad i = 1,\ldots,N-1.\end{aligned} \tag{44}$$

For linear multidimensional networks the noise is state independent, but correlations exist among the noise terms. Consider capacitor i and its two nearest neighbors $i - 1$ and $i + 1$: conservation of charge requires a fluctuation in the number of charges on i to be offset by an equal and opposite fluctuation of charges on the two nearest neighbors. Thus, the negative mixed partial derivative terms between nearest-neighbor capacitors exists because a fluctuation of charge on capacitor i requires the charge to be transferred from capacitor $i-1$ or $i+1$. This cross correlation is found for chemical reactions with more than one chemical intermediate species. If the multidimensional chemical master equation is approximated as a Fokker-Planck equation, then the probability diffusion coefficients are $\Gamma_{i,i} > 0$ and $\Gamma_{i,i-1} < 0$ and $\Gamma_{i,i+1} < 0$ [25].

C. Nonlinear one-dimensional circuits

We now turn to nonlinear systems which can have multiple stationary states. A nonlinear generalization of Eq. (15) is

$$\frac{dV_X}{dt} = \frac{V_A - V_X}{C(V_X)R_1(V_A,V_X)} - \frac{V_X - V_B}{C(V_X)R_2(V_X,V_B)} = -\frac{V_X - V_X^*}{C(V_X)}\left(\frac{1}{R_1(V_A,V_X)} + \frac{1}{R_2(V_X,V_B)}\right), \tag{45}$$

where

$$V_X^* = \left(\frac{V_A}{R_1(V_A,V_X)} + \frac{V_B}{R_2(V_X,V_B)}\right)\left(\frac{1}{R_1(V_A,V_X)} + \frac{1}{R_2(V_X,V_B)}\right)^{-1} = \left(\frac{V_A'}{R_1'} - \frac{V_B'}{R_2'}\right)\left(\frac{1}{R_1'} + \frac{1}{R_2'}\right)^{-1}. \tag{46}$$

V_X^* is the stationary state of the instantaneously equivalent linear electrical circuit (see Sec. II). For a given transfer of charge among V_A, V_X, and V_B, the change in energy of the system is

$$dE = V_A dn_A + V_X dn_X + V_B dn_B. \tag{47}$$

For an identical transfer of charge but at the voltage V_X^*, the stationary state of the ITKE linear system, the change in energy is

$$dE^* = V_A dn_A + V_X^* dn_X + V_B dn_B. \tag{48}$$

The difference defines the differential of the excess work $d\phi$,

$$d\phi = (V_X - V_X^*)dn_X = (V_X - V_X^*)C(V_X)dV_X. \tag{49}$$

Therefore, we have

$$\phi = \int (V_X - V_X^*)C_X(V_X)dV_X, \tag{50}$$

where V_X^* is a function of V_X, and the constant of integration is introduced such that $\phi \geq 0$. The time derivative of ϕ is

$$\frac{d\phi}{dt} = (V_X - V_X^*)C_X(V_X)\frac{dV_X}{dt} = -(V_X - V_X^*)^2\left(\frac{1}{R_1(V_A,V_X)} + \frac{1}{R_2(V_X,V_B)}\right). \tag{51}$$

Thus, ϕ decreases continually in time and is a Liapunov function. ϕ is also an extremum in the stationary state since

$$\left.\frac{\partial\phi}{\partial V_X}\right|_s = C_X(V_X)(V_X - V_X^*)\,|_s = -\dot{V}_X\left(\frac{1}{R_1(V_A,V_X)} + \frac{1}{R_2(V_X,V_B)}\right)^{-1} C(V_X)^2\,|_s = 0. \tag{52}$$

The second derivative evaluated at the stationary state gives necessary and sufficient stability properties,

$$\begin{aligned}\left.\frac{\partial^2\phi}{\partial V_X^2}\right|_s &= -\frac{\partial\dot{V}_X}{\partial V_X}\left(\frac{1}{R_1(V_A,V_X)} + \frac{1}{R_2(V_X,V_B)}\right)^{-1} C(V_X)^2 - \dot{V}_X\frac{\partial}{\partial V_X}\left.\left[\left(\frac{1}{R_1(V_A,V_X)} + \frac{1}{R_2(V_X,V_B)}\right)^{-1} C(V_X)^2\right]\right|_s \\ &= -\frac{\partial\dot{V}_X}{\partial V_X}\left(\frac{1}{R_1(V_A,V_X)} + \frac{1}{R_2(V_X,V_B)}\right)^{-1} C(V_X)^2\,|_s\,.\end{aligned} \tag{53}$$

Since the resistances and capacitances are always positive, the coefficient of the partial derivative is negative. Thus, if the stationary state is stable, then by linear stability analysis $\partial\dot{V}_X/\partial V_X < 0$ and ϕ is a minimum, and if the stationary state is unstable, then by linear stability analysis $\partial\dot{V}_X/\partial V_X > 0$ and ϕ is a maximum.

In the ITKE electric circuit corresponding to this nonlinear circuit, the dissipation is given by Eq. (24) and ϕ is related to the total dissipation by Eq. (25). In the nonlinear circuit the dissipation is

$$D = \frac{(V_A - V_X)^2}{R_1(V_A,V_X)} + \frac{(V_X - V_B)^2}{R_2(V_X,V_B)}. \tag{54}$$

At each instant the dissipation in the nonlinear circuit is identical to that in the ITKE circuit. However, unlike in the ITKE linear circuit the dissipation in a nonlinear circuit does not split into the dissipation at the stationary state and $\dot{\phi}$. The total dissipation can be rewritten as

$$D = \frac{(V_A - V_X^*)(V_A - V_X)}{R_1(V_A,V_X)} - \frac{(V_B - V_X^*)(V_X - V_B)}{R_2(V_X,V_B)} - \dot{\phi} \tag{55}$$

and $\dot{\phi}$ is again seen to be a component of the total dissipation. The component of the dissipation not represented by $\dot{\phi}$ is the dissipation that results from the transfer of charge from the battery at V_A to the capacitor at the voltage V_X^* at the rate $(V_A - V_X)/R_1(V_A, V_X)$ and the transfer of charge from the battery at V_B to the capacitor at the voltage V_X^* at the rate $(V_X - V_B)/R_2(V_X, V_B)$. The term $\dot{\phi}$ represents the dissipation due to the displacement of V_X from V_X^*. The dissipation is not necessarily minimized in the stationary state, but $\dot{\phi}$ is.

We again seek a stochastic equation for which the exponential of $-\phi$ is a solution of the stationary distribution. It is a Fokker-Planck equation [28]

$$\frac{\partial P}{\partial t} = -\frac{\partial f(V_X)P}{\partial V_X} + \frac{\partial}{\partial V_X}\Gamma\frac{\partial P}{\partial V_X}, \tag{56}$$

where $f(V_X)$ is the right-hand side of Eq. (45). The noise and the probability distribution are

$$\Gamma = \left(\frac{1}{R_1(V_A, V_X)} + \frac{1}{R_2(V_X, V_B)}\right)\frac{kT}{C_X(V_X)^2}, \tag{57}$$

$$P(V_X) \propto \exp(-\phi/kt). \tag{58}$$

In the nonlinear circuit, for ϕ to give a stationary solution of the Fokker-Planck equation, the amplitude of the noise must depend on the state variable V_X, but in a linear circuit the noise is state independent. This can be contrasted with the chemical case: the Fokker-Planck approximation of the chemical master equation contains state-dependent noise for both linear and nonlinear reactions (see discussion).

D. Nonlinear N-dimensional networks

The results of Secs. III B and III C generalize to nonlinear multidimensional circuits; however, as we will show, there is a significant difference: $d\phi$ is an exact differential for linear or one-variable systems but not generally so for nonlinear multidimensional circuits, and hence a path of integration must be defined. Consider the nonlinear generalization of Eq. (31),

$$\begin{aligned}\frac{dV_i}{dt} &= \frac{V_{i-1} - V_i}{C_i(V_i)R_i(V_{i-1}, V_i)} - \frac{V_i - V_{i+1}}{C_i(V_i)R_{i+1}(V_i, V_{i+1})} \\ &= -\frac{V_i - V_i^*}{C_i(V_i)}\left(\frac{1}{R_i(V_{i-1}, V_i)} + \frac{1}{R_{i+1}(V_i, V_{i+1})}\right) + \frac{V_{i-1} - V_{i-1}^*}{C_i(V_i)R_i(V_{i-1}, V_i)} + \frac{V_{i+1} - V_{i+1}^*}{C_i(V_i)R_{i+1}(V_i, V_{i+1})},\end{aligned} \tag{59}$$

where $1 \le i \le N$ and the (*) voltages are given by

$$\begin{aligned}V_i^* &= \left(\frac{V_{i-1}^*}{R_i(V_{i-1}, V_i)} + \frac{V_{i+1}^*}{R_{i+1}(V_i, V_{i+1})}\right)\left(\frac{1}{R_i(V_{i-1}, V_i)} + \frac{1}{R_{i+1}(V_i, V_{i+1})}\right)^{-1} \\ &= \left(\frac{V_{i-1}'^s}{R_i'} + \frac{V_{i+1}'^s}{R_{i+1}'}\right)\left(\frac{1}{R_i'} + \frac{1}{R_{i+1}'}\right)^{-1}.\end{aligned} \tag{60}$$

For a given transfer of charge, the change in the energy of the system is

$$dE = \sum_{i=0}^{N+1} V_i dn_i, \tag{61}$$

where dn_i denotes the transfer of charge at V_i. For an identical transfer of charge but at the (*) voltage,

$$dE^* = \sum_{i=0}^{N+1} V_i^* dn_i, \tag{62}$$

and the difference defines the differential $d\phi$ of the excess work

$$d\phi = \sum_{i=1}^{N}(V_i - V_i^*)dn_i = \sum_{i=1}^{N}(V_i - V_i^*)C_i(V_i)dV_i. \tag{63}$$

Our attention immediately turns to the fact that $d\phi$ is in general an inexact differential since V_i^* may depend on all the other capacitor voltages. The integral of Eq. (63),

$$\phi = \sum_{i=1}^{N}\int^{V_1,\ldots,V_N}(V_i - V_i^*)C_i(V_i)dV_i, \tag{64}$$

requires a path of integration. Hence, ϕ for a multidimensional nonlinear circuit is not in general a state function. We must augment Eq. (63) with a path of integration, and the value of ϕ at a given point depends on the path chosen. In Refs. [3] and [4] the authors show that the deterministic path is the proper choice for a variety of reasons,

$$\phi = \sum_{i=1}^{N}\int_{\infty}^{0}(V_i - V_i^*)C_i(V_i)\frac{dV_i}{dt}dt. \tag{65}$$

On a macroscopic level, they consider a bistable system; two stationary states separated by an unstable separatrix. They require that the value of ϕ, as a given point on the separatrix is approached from either basin of attraction, be independent of the stable stationary state chosen as the end point of the trajectory, except for a constant offset. This condition is met if the deterministic trajectory is used, but not if other paths such as a straight line are used. On a mesoscopic level, they use microscopic reversibility and Kurtz's theorem to show that the deterministic potential $\exp(-\phi_{\mathrm{det}}/RT)$ is the most probable path for fluctuations. Lastly, they show that the potential generated by $\exp(-\phi_{\mathrm{det}}/RT)$ is a useful approximation to the numerical solution of a master equation with a finite number of particles.

The proofs of properties (ii) and (iii) in Sec. I follow that given in Sec. III B; however, while ϕ is a minimum in the stationary state, the dissipation is not generally minimized in the stationary state, as is shown for the nonlinear one-dimensional circuit (Sec. III C).

E. Linear one-dimensional *LR* networks

We now turn our attention to circuits containing inductive elements. The only sources of dissipation are the resistances, however we allow an additional element which stores energy; the inductor. We do not treat *LR* and *LRC* networks as completely as *RC* networks, but we show that the RHH approach generalizes to inductive circuits.

A linear *LR* network is pictured in Fig. 4. The time dependence of the current through the circuit is

$$\frac{dI}{dt} = \frac{V_X - V_B}{L} = -\frac{R(I - I^s)}{L}, \tag{66}$$

where V_X is a function of time. The time derivative of ϕ from either Eq. (80) or (81) is

$$I^s = \frac{V_A - V_B}{R}. \tag{67}$$

The change in the energy stored in the magnetic field by the inductor for an incremental change in the current is $dE = LIdI$. For a given transfer of charge between V_A and V_B, the change in the energy of the system is

$$dE = V_A dn_A + V_B dn_B + LIdI. \tag{68}$$

Using the definition of current and conservation of charge we have $I = dn_A/dt = -dn_B/dt$, and thus Eq. (68) implicitly depends on time. This is contrasted with the *RC* circuits and the chemical case where dE or dM are independent of time. For an identical transfer of charge but at the stationary-state current we have

$$dE^s = V_A dn_A + V_B dn_B + LI^s dI, \tag{69}$$

and the difference of Eqs. (68) and (69) defines the differential $d\phi$ which is the excess work,

$$d\phi = L(I - I^s)dI. \tag{70}$$

Integration of Eq. (70) yields

$$\phi = \frac{L}{2}(I - I^s)^2, \tag{71}$$

and ϕ is greater than zero except at the stationary state, where it is zero.

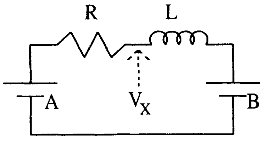

FIG. 4. The *LR* circuit used in Sec. III E.

The time derivative of ϕ,

$$\frac{d\phi}{dt} = L(I - I^s)\frac{dI}{dt} = -R(I - I^s)^2 = -\frac{(V_X - V_B)^2}{R}, \tag{72}$$

is always negative except at the stationary state, where it is zero. Thus, ϕ decreases to a minimum as the circuit evolves from an arbitrary state to a stationary state; it is a Liapunov function, and expresses the macroscopic driving force towards the stationary state. ϕ also gives necessary and sufficient stability properties of the stationary state,

$$\left.\frac{\partial\phi}{\partial I}\right|_s = L(I - I^s)\,|_s = 0, \quad \frac{\partial^2\phi}{\partial I^2} = L > 0, \tag{73}$$

and hence ϕ is a minimum in the stationary state and the stationary state is stable.

The power dissipated by the resistor is

$$D = RI^2 = \frac{(V_A - V_X)^2}{R} = D^s - \dot{\phi} + 2RI^s(I - I^s) \tag{74}$$

and thus $\dot{\phi}$ is a component of the total dissipation. Equation (74) indicates that the dissipation in a nonequilibrium stationary state of a linear inductive circuit is not a minimum [8, 11]. Assuming $V_A \neq V_B$, the dissipation increases monotonically from 0 as V_X varies from V_A (the minimum dissipation) to V_B (the stationary state). However, the component of the dissipation represented by $\dot{\phi}$ decreases monotonically as V_X approaches V_B.

We again assume there is a stochastic equation for which ϕ is a solution of the stationary probability distribution. We rewrite Eq. (66) as a Langevin equation

$$\frac{dI}{dt} = \frac{V_X - V_B}{L} = f(V_X) + \sqrt{2\Gamma}\epsilon. \tag{75}$$

The corresponding Fokker-Planck equation is

$$\frac{\partial P}{\partial t} = -\frac{\partial f(V_X)P}{\partial I} + \frac{\partial^2 \Gamma P}{\partial I^2}. \tag{76}$$

If we assume that $P \propto \exp(-\phi/kT)$, then the amplitude of the noise is

$$\Gamma = \frac{RkT}{L^2}. \tag{77}$$

As in the linear *RC* network, the amplitude of the noise is state independent.

F. Nonlinear *LRC* networks

In this subsection we combine inductive and capacitive networks to form a nonlinear *LRC* network as pictured in Fig. 5. The equations of motion for this network are

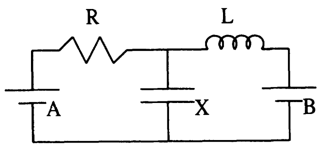

FIG. 5. The *LRC* circuit used in Sec. III F.

$$\begin{aligned}\frac{dI_2}{dt} &= \frac{V_X - V_B}{L(I_2)} = \frac{V_X - V_X^*}{L(I_2)},\\ \frac{dV_X}{dt} &= \frac{V_A - V_X}{R(V_A,V_X)C(V_X)} - \frac{I_2}{C(V_X)}\\ &= -\frac{V_X - V_X^*}{R(V_A,V_X)C(V_X)} - \frac{I_2 - I_2^*}{C(V_X)}.\end{aligned}\tag{78}$$

These equations have a unique stationary state of $V_X = V_B$ and $I_2 = (V_A - V_B)/R(V_A, V_B)$; the (*) states are the stationary states of the ITKE linear network

$$\begin{aligned}V_X^* &= V_B,\\ I_2^* &= \frac{V_A - V_B}{R(V_A,V_X)}.\end{aligned}\tag{79}$$

The differential of the excess work is given by

$$d\phi = (V_X - V_X^*)C(V_X)dV_X + (I_2 - I_2^*)L(I_2)dI_2, \tag{80}$$

which is an inexact differential since I_2^* depends on V_X. We define ϕ as the integral over the deterministic path

$$\begin{aligned}\phi &= \int_\infty^0 (V_X - V_X^*)C(V_X)\frac{dV_X}{dt} + (I_2 - I_2^*)L(I_2)\frac{dI_2}{dt}dt\\ &= \int_\infty^0 \left(\frac{(V_X - V_X^*)^2}{R(V_A,V_X)}\right)dt,\end{aligned}\tag{81}$$

where V_X is a function of time. The time derivative of ϕ from either Eq. (80) or (81) is

$$\begin{aligned}\frac{d\phi}{dt} &= (V_X - V_X^*)C(V_X)\frac{dV_X}{dt} + (I_2 - I_2^*)L(I_2)\frac{dI_2}{dt}\\ &= -\frac{(V_X - V_X^*)^2}{R(V_A,V_X)}.\end{aligned}\tag{82}$$

Thus ϕ decreases with time. ϕ can also be shown to be an extremum in a stationary state. Since ϕ decreases spontaneously with time, stable stationary states must be minima and unstable stationary states must be maxima.

Further properties of ϕ can be derived and they are similar to those found for one-dimensional *RC* circuits (Sec. III C). The circuit in Fig. 5 is capable of supporting sustained oscillations. We emphasize that the analysis presented here assumes only fixed-point attractors. The theory for limit-cycle attractors is in development.

In general, solving a nonlinear multidimensional Fokker-Planck equation is a difficult problem, so we examine the stochastic basis of ϕ for the linear case; $C(V_X) = C$, $R(V_A, V_X) = R$, and $L(I_2) = L$. We seek the stochastic equation for which $\exp(-\phi)$ gives the stationary probability distribution. If we write Eqs. (78) as Langevin equations, then

$$\begin{aligned}\frac{dI_2}{dt} &= \frac{V_X - V_B}{L} = f_1(V_X),\\ \frac{dV_X}{dt} &= \frac{V_A - V_X}{RC} - \frac{I_2}{C} + \sqrt{2\Gamma}\epsilon = f_2(V_X,I_2) + \sqrt{2\Gamma}\epsilon.\end{aligned}\tag{83}$$

The Fokker-Planck equation which corresponds to this Langevin equation is

$$\frac{\partial P}{\partial t} = -\frac{\partial f_1(V_X)P}{\partial I_2} - \frac{\partial f_2(V_X,I_2)P}{\partial V_X} + \Gamma\frac{\partial^2 P}{\partial V_X^2}. \tag{84}$$

If the stationary probability distribution is given by

$$P \propto \exp\left(\frac{C(V_X - V_X^*)^2 + L(I_2 - I_2^*)^2}{2kT}\right), \tag{85}$$

then

$$\Gamma = \frac{kT}{RC^2} \tag{86}$$

and thus the noise term only need appear in the differential equation for the capacitor voltage. The circuit interacts with the heat bath only through the resistor. Thus, the noise term in the Langevin Eqs. (83) is connected with the resistance terms and only appears in the equation for the capacitor voltage.

IV. COMPARISON WITH CHEMICAL SYSTEMS AND TRANSPORT PROCESSES

Using the RHH [1–4] approach we have discussed the thermodynamic and stochastic theory of a number of classes of electrical circuits. The same approach has been applied to chemical reactions, diffusion, thermal conduction, and Poiseuille and Couette fluid flow [5]. The results for electrical circuits are most similar to those for fluid flow, because changes of state variables in the electrical and fluid flow systems produce only changes of internal energy: kinetic energy for fluid flow and electromagnetic energy for circuits. The dissipation is equivalent to the loss of free energy, and the free energy has only energy terms, not entropy terms. However, in chemical reactions, heat conduction, and diffusion, changes of state involve both changes of internal energy and entropy. The dissipation is equivalent to the loss of free energy of the system, and free energy has both energy and entropy components.

Oster, Perelson, and Katchalsky [29–31] have developed a translation of chemical networks into generalized networks and with this translation an equivalent electrical network can be written for a chemical system. The electrical network is composed of nonlinear resistors, capacitors, and transformers. Chemical potentials are mapped to voltages on capacitors, and the reaction rates to currents through resistors. The power dissipated by the resistors is identical to that dissipated by the reaction mechanism. Linear chemical mechanisms translate to nonlinear circuits. Thus, ϕ for a chemical network differs from ϕ for the equivalent electrical network, since the ITKE system is different. Further, ϕ for a chemical network with concentration variables solves a master equation, but ϕ for a nonlinear electrical network solves a Fokker-Planck equation with state-dependent noise. In the presence of external noise large compared to internal noise, yet very small compared to macroscopic averages, this difference disappears [32].

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