

## Irreversible Thermodynamics of a Nonlinear $R$ - $C$ System

WILLIAM BERNARD

*Research Division, Raytheon Company, Waltham, Massachusetts*

AND

HERBERT B. CALLEN\*

*Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania*

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The formalism of nonlinear irreversible thermodynamics, as recently given by us, is applied to a circuit containing a capacitor and a nonlinear resistor. The solution is compared with those obtained by M. Lax and other investigators. It is shown that the fluctuation-dissipation theorem is rigorous, and that no correction factors need be introduced for nonlinear systems. The dynamical behavior of the microscopic fluctuations, from which the macroscopic motion can be obtained, is also derived. Finally, a specific Markoffian model of a nonlinear  $R$ - $C$  system, in strong interaction with a temperature reservoir, is shown to be consistent with the general analysis.

### INTRODUCTION

A REASONABLY satisfactory theory of irreversible thermodynamics of linear processes has been developed in recent years. It is natural that attention should then have shifted to the irreversible thermodynamics of nonlinear processes. An impetus to this extension arose from the importance of the excess noise associated with the current in an electrical system; the existence of this additional noise, above the equilibrium noise, is intimately associated with nonlinearity.<sup>1</sup>

In order to guide the development of a general theory of nonlinear irreversible thermodynamics, several investigators undertook the analysis of a specific nonlinear system. This system, composed simply of a capacitor and a nonlinear resistor in series, has been studied by MacDonald,<sup>2</sup> van Kampen,<sup>3</sup> and Davies.<sup>4</sup>

Recently the present authors have given a general formulation of nonlinear irreversible thermodynamics.<sup>1</sup> Lax,<sup>5</sup> in a recent comprehensive analysis of Markoff processes, has also devoted several sections to the nonlinear aspects of such processes. In addition, this nonlinear theory was applied by Lax to the nonlinear  $R$ - $C$  system. The results of MacDonald, van Kampen, and Davies can all be obtained from Lax's solution by introducing additional approximations, and we therefore adopt his as the basis of comparison. That solution appeared to be incompatible with our general analysis and to disagree with the fluctuation-dissipation theorem established in the linear theory.<sup>6,7</sup>

In this note we give a solution for the nonlinear  $R$ - $C$  system, which follows directly from our general formula-

tion and which agrees with the fluctuation-dissipation theorem. We also derive the dynamical behavior of the microscopic fluctuations, from which both the linear and nonlinear terms in the macroscopic response can be obtained, and we show how the macroscopic dynamical parameters can be identified from the microscopic transition probability. Finally, we consider a specific model of a Markoffian system in strong interaction with a temperature reservoir, to exhibit the explicit relationship between the microscopic and macroscopic dynamics of a nonlinear  $R$ - $C$  system.

The source of the apparent discrepancy between our results and those of Lax can be easily identified. As shown in Sec. 2, the macroscopic equation of motion for a nonlinear  $R$ - $C$  system involves various powers of the average value of the charge  $q$ :  $\langle q \rangle$ ,  $\langle q \rangle^2$ ,  $\langle q \rangle^3$ ,  $\dots$ . On the other hand, the Markoffian assumption adopted by Lax, as well as the earlier investigators, leads to an equation of motion having a similar form, except that  $\langle q \rangle^n$  is everywhere replaced by the  $n$ th charge moment  $\langle q^n \rangle$ . On the assumption that experimental measurement would be unlikely to distinguish between  $\langle q \rangle^n$  and  $\langle q^n \rangle$ , the coefficients in this equation were incorrectly identified with the capacitance and resistance.

As we shall see subsequently, a deeper origin of the discrepancy is the following. The macroscopic response of the system is easily written in terms of the initial voltage. This response is properly to be considered as the response to a given initial charge, averaged over the appropriate canonical distribution of initial charges consistent with the given voltage. Macroscopically the distinction between the response to a given initial charge and that to a given initial voltage is academic. But in considering the decay of a microscopic fluctuation the distinction becomes essential. Analysis of the microscopic dynamics is generally phrased in terms of the decay from a given initial charge deviation, and it is not proper to associate this directly with the macroscopic decay function. The difference lies precisely in the dis-

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<sup>1</sup> W. Bernard and H. B. Callen, *Revs. Modern Phys.* **31**, 1017 (1959).

<sup>2</sup> D. K. C. MacDonald, *Phys. Rev.* **108**, 541 (1957).

<sup>3</sup> N. G. van Kampen, *Phys. Rev.* **110**, 319 (1958).

<sup>4</sup> R. O. Davies, *Physica* **24**, 1055 (1958).

<sup>5</sup> M. Lax, *Revs. Modern Phys.* **32**, 25 (1960). We are indebted to Dr. Lax for a prepublication copy of this work.

<sup>6</sup> H. B. Callen and T. A. Welton, *Phys. Rev.* **83**, 34 (1951).

<sup>7</sup> H. B. Callen, M. L. Barasch, and J. L. Jackson, *Phys. Rev.* **88**, 1382 (1952).

inction between  $\langle q^n(t) \rangle$  and  $\langle q(t) \rangle^n$ , as we shall demonstrate in the following sections.

2. THE THERMODYNAMIC SOLUTION

If a circuit contains a linear capacitor and a nonlinear resistor, Kirchoff's law gives

$$\frac{d}{dt}\langle q(t) \rangle + \frac{V(t)}{R[V(t)]} = 0, \tag{1}$$

where

$$V(t) = \langle q(t) \rangle / C, \tag{2}$$

and where  $R$  is a general function of  $V(t)$ .

The surprising feature of the Lax solution (see Sec. 4) is that the equilibrium second correlation moment  $\langle qq(t) \rangle^{(0)}$  is found to involve the coefficients of the higher-power terms in the expansion of  $R$  in a power series in  $V$ . On the other hand, the fluctuation-dissipation theorem, and our general formulation of nonlinearity, relate the equilibrium second moment to the zero-order term in the expansion of  $R(V)$ , independently of the higher-order terms.

The relevant theorem of our general approach, on which we base our analysis of the nonlinear  $R$ - $C$  circuit, is as follows. Consider a system which prior to  $t=0$  is in generalized canonical equilibrium with respect to a temperature  $T$  and a constant imposed intensive parameter  $V$ . At  $t=0$  the generalized force  $V$  is removed, and the system then relaxes into its new equilibrium configuration. The expectation value  $\langle q(t) \rangle$  at time  $t$  of the extensive variable  $q$  conjugate to  $V$  can be expanded, in the classical limit of large  $T$ , as<sup>1</sup>

$$\langle q(t) \rangle = (V/kT)\langle qq(t) \rangle^{(0)} + \frac{1}{2}(V/kT)^2\langle q^2q(t) \rangle^{(0)} + \frac{1}{6}(V/kT)^3 \times [\langle q^3q(t) \rangle^{(0)} - 3\langle q^2 \rangle^{(0)}\langle qq(t) \rangle^{(0)}] + \dots \tag{3}$$

The bracket  $\langle \rangle^{(0)}$  denotes an expectation value with respect to the unperturbed equilibrium ensemble. (For simplicity we have assumed  $q$  to be defined such that  $\langle q \rangle^{(0)} = 0$ .) Thus, the equilibrium second correlation moment  $\langle qq(t) \rangle^{(0)}$  is uniquely determined by the linear term in the response  $\langle q(t) \rangle$ , the equilibrium third correlation moment  $\langle q^2q(t) \rangle^{(0)}$  by the second-order response, etc.

In order to specialize the result given in Eq. (3) to the system in which we are interested, it is necessary to solve the macroscopic equation of motion [Eq. (1)]. For the sake of illustration we shall consider explicitly the case in which

$$R(V) = R_0 + R_1V + R_2V^2. \tag{4}$$

Then Eq. (1) becomes

$$\frac{d}{dt}\langle q(t) \rangle + \frac{\langle q(t) \rangle}{R_0C + R_1\langle q(t) \rangle + (R_2/C)\langle q(t) \rangle^2} = 0. \tag{5}$$

For later reference we note that the series expansion of this equation is

$$\begin{aligned} \frac{d}{dt}\langle q(t) \rangle = & -\frac{1}{R_0C}\langle q(t) \rangle + \frac{R_1}{R_0^2C^2}\langle q(t) \rangle^2 \\ & + \left( \frac{R_2}{R_0^3C^3} - \frac{R_1^2}{R_0^3C^3} \right) \langle q(t) \rangle^3 + \dots \end{aligned} \tag{6}$$

The solution of Eq. (5) is

$$\begin{aligned} R_0C \ln \frac{\langle q(t) \rangle}{\langle q(0) \rangle} + R_1[\langle q(t) \rangle - \langle q(0) \rangle] \\ + \frac{R_2}{2C}[\langle q(t) \rangle^2 - \langle q(0) \rangle^2] = -t, \end{aligned} \tag{7}$$

where  $\langle q(0) \rangle$  is the expectation value of  $q$  at time zero. If we expand  $\langle q(t) \rangle$  in a power series in  $\langle q(0) \rangle$ , insert this series into Eq. (7), expand the logarithm, and equate the coefficients of the various powers of  $\langle q(0) \rangle$  to zero, we find

$$\begin{aligned} \langle q(t) \rangle = & \langle q(0) \rangle e^{-t/R_0C} + \langle q(0) \rangle^2 (R_1/R_0C) [e^{-t/R_0C} - e^{-2t/R_0C}] \\ & + \langle q(0) \rangle^3 (1/2R_0^2C^2) [(R_1^2 + R_0R_2)e^{-t/R_0C} \\ & - 4R_1^2e^{-2t/R_0C} + (3R_1^2 - R_0R_2)e^{-3t/R_0C}]. \end{aligned} \tag{8}$$

Recalling that  $\langle q(0) \rangle = CV$  and comparing with Eq. (3), we identify the various equilibrium correlation moments.

$$\langle qq(t) \rangle^{(0)} = kTC e^{-t/R_0C}, \tag{9}$$

$$\langle q^2q(t) \rangle^{(0)} = 2(kTC)^2 (R_1/R_0C^2) [e^{-t/R_0C} - e^{-2t/R_0C}], \tag{10}$$

$$\begin{aligned} \langle q^3q(t) \rangle^{(0)} = & 3(kTC)^2 \{ e^{-t/R_0C} + (kTC/R_0^2C^2) \\ & \times [(R_1^2 + R_0R_2)e^{-t/R_0C} - 4R_1^2e^{-2t/R_0C} \\ & + (3R_1^2 - R_0R_2)e^{-3t/R_0C}] \}. \end{aligned} \tag{11}$$

Thus, we find that, even in the presence of the nonlinearity, the second correlation moment  $\langle qq(t) \rangle^{(0)}$  is identical to that of a linear  $R$ - $C$  system. In order to find any effect of the nonlinearity on the behavior of the equilibrium fluctuations it is necessary to consider higher equilibrium correlation moments.

It is of interest to note that at  $t=0$  the equilibrium fluctuation moments reduce to those obtained from the linear static characteristic  $\langle q \rangle = CV$ , using conventional thermostatic fluctuation theory.<sup>8</sup>

$$\langle q^2 \rangle^{(0)} = kTC, \tag{12}$$

$$\langle q^3 \rangle^{(0)} = 0, \tag{13}$$

$$\langle q^4 \rangle^{(0)} = 3(kTC)^2. \tag{14}$$

Equations (12)-(14) imply the Gaussian equilibrium probability distribution.

$$W^{(0)}(q) = [1/(2\pi kTC)^{1/2}] \exp(-q^2/2kTC). \tag{15}$$

Hence, we differ with Lax,<sup>5</sup> who asserts that, especially when odd nonlinearities are present, Eq. (15) cannot be valid.

<sup>8</sup> R. F. Greene and H. B. Callen, Phys. Rev. 83, 1231 (1951).

### 3. REGRESSION OF EQUILIBRIUM FLUCTUATIONS

In general, the macroscopic motion of a system is built up in some complicated way from the microscopic regression of equilibrium fluctuations. At least in the simple example considered, however, it is possible to determine a microscopic behavior which in fact gives rise to the equilibrium fluctuation moments obtained above from the macroscopic motion.

We assume that the equilibrium fluctuations regress in a nonlinear way according to

$$\langle q(t) \rangle_{q'}^{(0)} = L_0(t) + q' L_1(t) + q'^2 L_2(t) + q'^3 L_3(t) + \dots, \quad (16)$$

where  $\langle q(t) \rangle_{q'}^{(0)}$  denotes the equilibrium expectation value of  $q$  at time  $t$  conditional on the value  $q'$  at time zero. The various equilibrium fluctuation moments given in Eqs. (9) through (11) can be obtained from Eq. (16) by multiplying through by the appropriate power of  $q'$  and averaging over the equilibrium probability distribution  $W^{(0)}(q')$ . Thus,

$$\langle qq(t) \rangle^{(0)} = \langle q^2 \rangle^{(0)} L_1(t) + \langle q^4 \rangle^{(0)} L_3(t), \quad (17)$$

$$\langle q^2 q(t) \rangle^{(0)} = \langle q^2 \rangle^{(0)} L_0(t) + \langle q^4 \rangle^{(0)} L_2(t), \quad (18)$$

$$\langle q^3 q(t) \rangle^{(0)} = \langle q^4 \rangle^{(0)} L_1(t) + \langle q^6 \rangle^{(0)} L_3(t). \quad (19)$$

The equilibrium first moment  $\langle q \rangle^{(0)} (=0)$  is obtained by averaging Eq. (16) directly.

$$\langle q \rangle^{(0)} = 0 = L_0(t) + \langle q^2 \rangle^{(0)} L_2(t). \quad (20)$$

Using Eqs. (9) and (11) for  $\langle qq(t) \rangle^{(0)}$  and  $\langle q^3 q(t) \rangle^{(0)}$ , respectively, and noting that  $\langle q^6 \rangle^{(0)} = 15(kTC)^3$ , Eqs. (17) and (19) can be solved for  $L_1(t)$  and  $L_3(t)$ . Similarly, Eqs. (18) and (20) can be solved for  $L_0(t)$  and  $L_2(t)$ . Substituting the results into Eq. (16), we obtain

$$\begin{aligned} \langle q(t) \rangle_{q'}^{(0)} = & - (kTR_1/R_0) (e^{-t/R_0C} - e^{-2t/R_0C}) \\ & + q' \{ e^{-t/R_0C} - (3kT/2R_0^2C) \\ & \times [(R_1^2 + R_0R_2)e^{-t/R_0C} - 4R_1^2 e^{-2t/R_0C} \\ & + (3R_1^2 - R_0R_2)e^{-3t/R_0C}] \} \\ & + q'^2 (R_1/R_0C) (e^{-t/R_0C} - e^{-2t/R_0C}) \\ & + q'^3 (1/2R_0^2C^2) [(R_1^2 + R_0R_2)e^{-t/R_0C} \\ & - 4R_1^2 e^{-2t/R_0C} \\ & + (3R_1^2 - R_0R_2)e^{-3t/R_0C}] + \dots \quad (21) \end{aligned}$$

Equation (21) for  $\langle q(t) \rangle_{q'}^{(0)}$  is qualitatively similar to the results obtained by previous workers<sup>2-5</sup> in that the linear term in  $q'$ , as well as the higher-order terms, depends on the nonlinearity of the system. However, our result differs in the important respect that the regression of equilibrium fluctuations is just such as to give rise to the second moment  $\langle qq(t) \rangle^{(0)}$  of Eq. (9), which is completely independent of the nonlinearity.

In considering a specific physical problem, it is customary to proceed from the microscopic equations of motion, constructing an appropriate macroscopic behavior from their solution. This, of course, is just the reverse of the approach we have adopted in the fore-

going theory. The question then arises as to whether a given microscopic model corresponds macroscopically to a nonlinear  $R$ - $C$  system or to some other type of system. The relevant criterion with respect to the microscopic motion is that it exhibit the form of Eq. (21). The macroscopic dynamical parameters can then be identified from the specific solution obtained for  $\langle q(t) \rangle_{q'}^{(0)}$  by comparing its power series expansion in  $q'$  with Eq. (21). However,  $R_0$ ,  $R_1$ , and  $R_2$  can also be obtained directly from the first moment of the microscopic transition probability (see also Sec. 4) as follows.  $\langle q(t) \rangle_{q'}^{(0)}$  can be written in terms of the equilibrium conditional probability distribution  $P^{(0)}(q'|q, t)$  as

$$\langle q(t) \rangle_{q'}^{(0)} = \int dq q P^{(0)}(q'|q, t). \quad (22)$$

Differentiating with respect to  $t$  and letting  $t \rightarrow 0$ , this becomes

$$\langle \dot{q} \rangle_{q'}^{(0)} = \int dq q \dot{P}^{(0)}(q'|q), \quad (23)$$

where

$$\dot{P}^{(0)}(q'|q) = \lim_{t \rightarrow 0} \frac{\partial}{\partial t} P^{(0)}(q'|q, t)$$

is just the probability per unit time of making a transition from  $q'$  to  $q$ . The series expansion of the left-hand side of Eq. (23) can be obtained from Eq. (21). Thus,

$$\begin{aligned} & \int dq q \dot{P}^{(0)}(q'|q) \\ & = - \frac{kTR_1}{R_0} - q' \frac{1}{R_0C} \left[ 1 + \frac{3kT}{R_0^2C} (R_0R_2 - R_1^2) \right] \\ & \quad + q'^2 \frac{R_1}{R_0C} + q'^3 \frac{1}{2R_0^2C} (R_0R_2 - R_1^2) + \dots \quad (24) \end{aligned}$$

### 4. MOTION OF A MARKOFFIAN SYSTEM

In order to effect a comparison between our results and those of other authors, we briefly discuss Lax's recent work.<sup>5</sup> The Markoffian assumption regarding the equilibrium conditional probability distribution  $P^{(0)}(q|q', t)$  implies the Chapman-Kolmogoroff relation

$$W(q, t + \Delta t) = \int dq' W(q', t) P^{(0)}(q|q', \Delta t), \quad (25)$$

where  $W(q, t)$  is the path distribution function for  $q$  during the relaxation process. Expanding in  $\Delta t$  and taking the limit  $\Delta t \rightarrow 0$ , this leads to the transport type of equation

$$\frac{\partial}{\partial t} W(q, t) = \int dq' W(q', t) \dot{P}^{(0)}(q'|q), \quad (26)$$

where  $\dot{P}^{(0)}(q'|q)$  is the previously defined microscopic transition probability.

Equation (26) can be used to compute the time derivatives of the various moments  $\langle q^n(t) \rangle$  of  $q$  in the nonequilibrium system characterized by  $W(q,t)$ . Thus, after some manipulation,

$$\frac{d}{dt}\langle q(t) \rangle = \int dq W(q,t) \int dq' (q'-q) \dot{P}^{(0)}(q|q'), \quad (27)$$

$$\begin{aligned} \frac{d}{dt}\langle q^2(t) \rangle &= \int dq W(q,t) \int dq' (q'-q)^2 \dot{P}^{(0)}(q|q') \\ &+ 2 \int dq q W(q,t) \\ &\times \int dq' (q'-q) \dot{P}^{(0)}(q|q'), \quad (28) \end{aligned}$$

...

Lax chooses to expand the moments of  $\dot{P}^{(0)}(q|q')$  in terms of a new variable  $\alpha = q - q_0$ , such that  $\int dq' (q' - q_0) \dot{P}^{(0)}(q_0|q') = 0$ .

$$\int dq' (q' - q) \dot{P}^{(0)}(q|q') = -\Lambda\alpha - B\alpha^2 - \Gamma\alpha^3 + \dots, \quad (29)$$

$$\frac{1}{n!} \int dq' (q' - q)^n \dot{P}^{(0)}(q|q') = D_n + E_n\alpha + F_n\alpha^2 + \dots, \quad (30)$$

which yields Eqs. (27), (28), ... in the form,<sup>9</sup>

$$\frac{d}{dt}\langle \alpha(t) \rangle = -\Lambda\langle \alpha(t) \rangle - B\langle \alpha^2(t) \rangle - \Gamma\langle \alpha^3(t) \rangle + \dots, \quad (31)$$

$$\begin{aligned} \frac{d}{dt}\langle \alpha^2(t) \rangle &= 2D_2 + 2E_2\langle \alpha(t) \rangle - 2(\Lambda - F_2)\langle \alpha^2(t) \rangle \\ &- 2B\langle \alpha^3(t) \rangle + \dots. \quad (32) \end{aligned}$$

We note that the variable  $\alpha \neq q - \langle q \rangle^{(0)}$  except in the lowest-order approximation; however, all Lax's results can be easily rewritten in terms of the more conventional variable  $q - \langle q \rangle^{(0)}$ . The equation of motion (31) differs from the conventional equation of motion (6) in that the quantities  $\langle q(t) \rangle^n$  are replaced by  $\langle q^n(t) \rangle$ , but Lax identifies  $\Lambda$  with  $1/R_0C$ ,  $B$  with  $-R_1/R_0^2C^2$ , and  $\Gamma$  with  $(-R_2/R_0^2C^3) + (R_1^2/R_0^3C^3)$ .

The coupled equations of motion (31), (32), ... are satisfied by solutions of the form  $\Delta\langle \alpha^n(t) \rangle = \langle \alpha^n(t) \rangle - \langle \alpha^n \rangle^{(0)} = e^{-\lambda_n t}$ ,  $\langle \alpha^n \rangle^{(0)}$  being the equilibrium component of  $\langle \alpha^n(t) \rangle$ . The eigenvalues  $\lambda_n$ , which in the absence of

<sup>9</sup> Because Lax's equations of motion depend solely upon the Markoffian assumption, they are equally valid for motion about a nonequilibrium steady-state operating point. Since it is not yet possible to make meaningful thermodynamic statements regarding this situation, however, we restrict ourselves here to the case of equilibrium operating points.

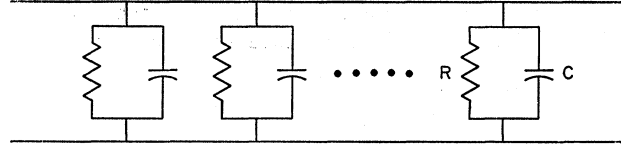


FIG. 1. A nonlinear  $R$ - $C$  system connected with a large number of identical systems.

the nonlinearity reduce to  $n\Lambda$ , are obtained by a perturbation technique to any desired order. Thus, the response  $\langle \alpha(t) \rangle$  can be expanded according to

$$\langle \alpha(t) \rangle = \langle \alpha \rangle^{(0)} + \sum_{n=1}^{\infty} a_n e^{-\lambda_n t}. \quad (33)$$

The coefficients  $a_n$  are determined in principle by the initial conditions of the problem, although the determination of more than two is complicated in practice by the non-Hermitian nature of the eigenvalue matrix. The equilibrium second correlation moment  $\langle \alpha\alpha(t) \rangle^{(0)}$  is obtained by assuming the initial probability distribution  $W(\alpha,0) = \delta(\alpha - \alpha')$ , multiplying Eq. (32) by  $\alpha'$ , and averaging over the equilibrium distribution  $W^{(0)}(\alpha')$ .

If the initial  $\delta$ -function distribution is used to determine the first two expansion coefficients  $a_1$  and  $a_2$ , Eq. (33) for  $\langle q(t) \rangle_{q'}$  assumes the form

$$\begin{aligned} \langle q(t) \rangle_{q'} &= q' e^{-\lambda_1 t} \\ &+ (f + bq' + cq'^2 + dq'^3) (e^{-\lambda_1 t} - e^{-\lambda_2 t}), \quad (34) \end{aligned}$$

where we have expressed Lax's results in terms of our variable  $q$ . The quantities  $b$ ,  $c$ ,  $d$ , and  $f$ , and also the  $\lambda$ 's, are functions of  $\Lambda$ ,  $B$ ,  $\Gamma$ , and the expansion coefficients of the higher moments of  $\dot{P}^{(0)}(q|q')$  given in Eq. (30). The equilibrium second moment  $\langle qq(t) \rangle^{(0)}$  obtained from Eq. (34) is

$$\begin{aligned} \langle qq(t) \rangle^{(0)} &= \langle q^2 \rangle^{(0)} e^{-\lambda_1 t} + (b\langle q^2 \rangle^{(0)} + c\langle q^3 \rangle^{(0)}) \\ &+ d\langle q^4 \rangle^{(0)} (e^{-\lambda_1 t} - e^{-\lambda_2 t}). \quad (35) \end{aligned}$$

One finds that  $(b\langle q^2 \rangle^{(0)} + c\langle q^3 \rangle^{(0)} + d\langle q^4 \rangle^{(0)})$  does not vanish identically, even if we admit the probability distribution  $W^{(0)}(q)$  of Eq. (15). We conclude that such a Markoffian system will in general not be equivalent to a nonlinear  $R$ - $C$  system.

## 5. A SPECIFIC MODEL

In order to illustrate the relationship between the microscopic and macroscopic behavior in concrete form we now consider a specific model. In particular we focus on one nonlinear  $R$ - $C$  system connected in parallel with a large number of identical replicas, as shown in Fig. 1. In addition the ensemble is assumed to be in strong interaction with a temperature reservoir.

If all the capacitors in the ensemble are charged, and the entire ensemble is permitted to relax to equilibrium, each system finds itself in continual quasi-static equilibrium with both a thermal reservoir and a "voltage reservoir." The voltage of this reservoir varies with time according to the macroscopic Eqs. (1) and (2). The

microscopic distribution function of the system is, then, the standard generalized canonical distribution<sup>1</sup>

$$W(q,t) = W^{(0)}(q) e^{V(t) q / kT} / \langle e^{V(t) q / kT} \rangle^{(0)} \\ = W^{(0)}(q) e^{q(t) q / kTC} / \langle e^{q(t) q / kTC} \rangle^{(0)}. \quad (36)$$

The equation of motion satisfied by  $W(q,t)$  is obtained by differentiating with respect to  $t$ .

$$\dot{W}(q,t) = (1/kTC) W(q,t) [\langle \dot{q}(t) \rangle q - \langle \dot{q}(t) \rangle \langle q(t) \rangle]. \quad (37)$$

Multiplying through by  $q$  and averaging over  $W^{(0)}(q)$ , we obtain an expression for  $d\langle q(t) \rangle / dt$  which yields the relation

$$\langle q^2(t) \rangle = \langle q(t) \rangle^2 + \langle q^2 \rangle^{(0)}. \quad (38)$$

Invoking Eq. (38), a similar calculation of  $d\langle q^2(t) \rangle / dt$  yields the relation

$$\langle q^3(t) \rangle = \langle q(t) \rangle^3 + 3\langle q^2 \rangle^{(0)} \langle q(t) \rangle. \quad (39)$$

The results expressed by Eqs. (38) and (39) clearly suffice to reduce the Markoffian equation of motion (31)

to the desired form, Eq. (6). Rewritten in terms of the variable  $q$  rather than Lax's variable  $\alpha$ , Eq. (31) becomes

$$\frac{d}{dt} \langle q(t) \rangle = A - \Lambda' \langle q(t) \rangle - B' \langle q^2(t) \rangle - \Gamma' \langle q^3(t) \rangle + \dots \quad (40)$$

Substituting Eqs. (38) and (39), we obtain

$$\frac{d}{dt} \langle q(t) \rangle = [A - B' \langle q^2 \rangle^{(0)}] - [\Lambda' + 3\Gamma' \langle q^2 \rangle^{(0)}] \langle q(t) \rangle \\ - B' \langle q(t) \rangle^2 - \Gamma' \langle q(t) \rangle^3 + \dots, \quad (41)$$

which is of the form of Eq. (6) with  $[A - B' \langle q^2 \rangle^{(0)}] = 0$ ,  $[\Lambda' + 3\Gamma' \langle q^2 \rangle^{(0)}] = 1/R_0 C$ ,  $B' = -R_1/R_0^2 C^2$ ,  $\Gamma' = -[(R_2/R_0^2 C^3) - (R_1^2/R_0^3 C^3)]$ . This identification of the coefficients is to be contrasted with that which would result from a direct comparison of Eqs. (6) and (40), ignoring the distinction between  $\langle q^n(t) \rangle$  and  $\langle q(t) \rangle^n$  [see also the discussion following Eq. (32)].

## Internal Field Emission at Narrow $p$ - $n$ Junctions in Indium Antimonide

A. G. CHYNOWETH AND R. A. LOGAN  
Bell Telephone Laboratories, Murray Hill, New Jersey  
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An experimental study has been made of the field and temperature dependence of internal field emission in narrow  $p$ - $n$  junctions in indium antimonide. Relatively good agreement, both qualitative and quantitative, is obtained between the experimental results and the usual expression for the barrier transparency. From studies of Esaki characteristics at low temperatures and from the observed temperature dependence of the tunnelling current, it is confirmed that the tunnelling transitions do not involve phonons. Also, it is shown that the temperature dependence of the barrier transparency is determined by that of the energy gap at  $k=0$ .

### INTRODUCTION

THE theoretical expression for the field dependence of the probability of internal field emission (tunnelling) is dominated by the factor<sup>1</sup>

$$\exp(-\alpha \epsilon^3 / E), \quad (1)$$

where, for direct transitions,

$$\alpha = \pi(m^*)^{3/2} / 2e\hbar,$$

and for indirect transitions,

$$\alpha = 4(2m^*)^{3/2} / 3e\hbar,$$

$\epsilon$  is the energy gap (direct or indirect, as appropriate),  $E$  is the electric field,  $m^*$  is an effective mass,  $e$  is the electron charge, and  $\hbar$  is  $h/2\pi$ , where  $h$  is Planck's con-

stant. Chynoweth et al.<sup>2</sup> have recently made an experimental study of tunnelling in narrow silicon and germanium junctions and in particular, they have verified that Eq. (1) satisfactorily describes, both qualitatively and quantitatively, the field dependence of the tunnel current at a given temperature. They also investigated the temperature dependence of the tunnel current. The form of the temperature dependence depends on whether the tunnelling transitions are direct or indirect, the latter requiring the absorption or emission of phonons. In semiconductors where the minimum energy gap lies at  $k=0$ , tunnelling of carriers between the two bands occurs by direct transitions. In this case the temperature dependence of the tunnel current is determined primarily by that of the energy gap. In those materials where the minimum energy gap does not occur at  $k=0$ , tunnelling may occur by indirect transi-

<sup>1</sup> F. V. Keldysh, J. Exptl. Theoret. Phys. (U.S.S.R.) **33**, 994 (1957), and **34**, 962 (1958) [translations: Soviet Phys. JETP **6**, 763 (1958), and **7**, 665 (1958), respectively].

<sup>2</sup> A. G. Chynoweth, W. L. Feldmann, C. A. Lee, R. A. Logan, G. L. Pearson and P. Aigrain (in press).