Irreversible thermodynamics of nonlinear transport processes and instability: Application to the current fluctuation phenomena in semiconductors

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Irreversible thermodynamics of nonlinear transport processes and Instability: Application to the current fluctuation phenomena in semiconductors[a)]

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The kinetic and irreversible thermodynamic theory for nonlinear transport processes reported previously is applied to study implication of a nonmonotonic entropy production with a specific example of the current fluctuations observed in the GaAs semiconductor. The study shows evidence that there is a connection between the nonmonotonicity in the entropy production and the instability phenomenon observed, which may be generic to nonlinear processes in macroscopic systems. It is proposed that the current fluctuations in GaAs is basically due to a bifurcation phenomenon in the current-field characteristic, as the field strength is increased past a critical value.

I. INTRODUCTION

The aim of the present paper is twofold: One is to study irreversible thermodynamics of nonlinear transport processes and associated instability with a specific example and the other is to study instability phenomena[1] occurring in semiconductors which are related to the Gunn oscillation.[2–4] We thereby hope to gain insight into irreversible thermodynamics of systems which require nonlinear dynamical descriptions. We will propose a mechanism for the current instability observed in semiconductors.

In linear irreversible thermodynamics[5] the entropy production is generally given as a sum of bilinear products of thermodynamic forces and conjugate fluxes. When linear phenomenological relations are used between the fluxes and forces, the entropy production may be expressed as a quadratic form either in fluxes or in forces, depending on our preference and the circumstances. The quadratic form in fluxes acts as if it is a "potential" and, when differentiated, yields the dissipative terms in the flux evolution equations, which produce stable solutions at equilibrium. The equilibrium state then is said to be stable since the system perturbed out of the equilibrium state returns to it without fail. This is a well-known characteristic of linear irreversible processes with a quadratic (Rayleigh–Onsager) dissipation function[6] or an entropy production quadratic in fluxes or forces. Therefore, a system described by linear evolution equations within linear irreversible thermodynamics is thermodynamically stable. A special emphasis must be put on the word *linear*. Note also that such systems are near thermodynamic equilibrium.

If the system is removed far from equilibrium, it is expected that linear irreversible thermodynamics is no longer able to describe properly the processes occurring in it, and the Rayleigh–Onsager dissipation function loses its usefulness. Onsager's theory[6(b)] of irreversible thermodynamics, nevertheless, appears to provide viewpoints in the right direction and a theoretical frame of reference for a possible nonlinear theory. Therefore, it seems logical to look for a generalization of the Rayleigh–Onsager dissipation function or its analog and examine its utility.

A recent series[7] of kinetic theory studies on irreversible thermodynamics of nonlinear transport processes has shown a way to generalize the theory of linear irreversible thermodynamics to the nonlinear regime. Among many other useful notions and equations suggested by the studies are the extended Gibbs relation for entropy density $\mathscr{S}$:

$$T d\mathscr{S} = d\mathscr{E} + p dv - \sum_i \hat{\mu}_i \, dc_i + \sum_{i\alpha} X_i^{(\alpha)} \odot d\hat{\Phi}_i^{(\alpha)} \quad (1.1)$$

and a formula for the entropy production σ:

$$\sigma = T^{-1} \sum_{i\alpha} X_i^{(\alpha)} \odot \Lambda_i^{(\alpha)}, \quad (1.2)$$

where T is the temperature, $\mathscr{E}$ the internal energy density, p the hydrostatic pressure, v the specific volume per unit mass, $\hat{\mu}_i$ the chemical potential per unit mass, c_i the mass fraction, $X_i^{(\alpha)}$ the generalized force, $\hat{\Phi}_i^{(\alpha)}$ the flux density, examples of which are the mass fluxes, heat fluxes, stress tensors, etc. to be defined later, and finally $\Lambda_i^{(\alpha)}$, the dissipative term in the evolution equation for $\hat{\Phi}_i^{(\alpha)}$. For further details the reader is referred to Ref. 7. In view of Eq. (1.1) we may write

$$X_i^{(\alpha)} = T(\partial \mathscr{S} / \partial \hat{\Phi}_i^{(\alpha)})_{\mathscr{E}, v, c_j, \hat{\Phi}_j^{(\gamma)}}, \quad (j \neq i, \gamma \neq \alpha). \quad (1.3)$$

Since the entropy is a function of the Gibbs variables $(\mathscr{E}, v, c_i, \hat{\Phi}_i^{(\alpha)}; i = 1,2,..., \alpha = 1.2,...)$, $X_i^{(\alpha)}$ are also functions of them. We shall have more precise mathematical forms for them in a later section. The form (1.2) for σ reminds us of the bilinear form for the entropy production in linear irreversible thermodynamics to which it reduces as the magnitudes of the fluxes diminish and thus the system approaches the equilibrium. The dissipative terms $\Lambda_i^{(\alpha)}$ are generally nonlinear functions of fluxes and are responsible for various nonlinear characteristics of processes not seen in the linear theory. In the kinetic theory approach they may be evaluated in terms of molecular parameters and various macroscopic variables.

In the present paper we will reverse the procedure used in the kinetic theory approach and assume forms for $\Lambda_i^{(\alpha)}$ for diffusion processes of two charged species, e.g., electrons or

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carriers, which are coupled nonlinearly. The forms for $\Lambda_i^{(\alpha)}$ are chosen so as to fulfill the requirement of the second law of thermodynamics by demanding that they yield collectively a nonnegative entropy production. They have features quite distinctive from the dissipation function of Rayleigh and Onsager. Most importantly, they are not monotonic functions of fluxes and therefore the corresponding entropy production is not monotonic for some parameter sets. The nonmonotonicity[8] in the entropy production appears to be related to certain features generic to nonlinear transport processes, and we wish to demonstrate their connection by carrying out calculations with a practical example. This way, and when enough evidence is gathered through similar studies, we will be able to arrive at a theory on the structure of entropy production and its relation to nonlinear transport processes, and thereby deduce the structure of the all important entropy of the system from experimental data on nonlinear transport processes. Thus, the present study represents a step in that direction.

As an example for making connection with experiment, we shall study the negative differential mobility and related instability phenomena observed in some semiconductors.[1-4] In particular, Kabashima *et al.*[1] experimentally observed that under certain conditions the GaAs semiconductor produces noisy fluctuating currents, when it is subjected to a bias voltage larger than a critical value. We show that the evolution equations presented and studied here produce not only the negative differential mobility associated with the Gunn effect, but also a switching branch of the steady state solution for the current–voltage characteristic. This branch of solution corresponds to a sudden increase in the current as the voltage is above the critical value. This sudden increase amounts in effect to an electrical switching—and this is associated with the particular feature of the entropy production postulated for the process in hand. These aspects are discussed in this paper.

Section II is for a brief review of the theory of nonlinear irreversible thermodynamics forming the foundation of the present work and for describing the underlying microscopic model for the phenomena in hand. In Sec. III linear stability analysis of steady states and a graphical method of analyzing the steady state structures are discussed. The graphical method, when combined with the stability analysis, provides considerable insights into the behavior of solutions without knowledge of the actual analytic form of the solution. In Sec. IV a special case of the parameter set is assumed and the experimental data are explicitly studied. A mechanism for fluctuating currents is proposed based on the study. It is different from the existing ones, as it is based on bifurcation theory. Section V is for discussion and conclusion.

II. EVOLUTION EQUATIONS

Evolution of macroscopic fluxes in space and time is subject to the requirement of thermodynamic laws. In the previous papers of this series it was discussed how one may derive from appropriate kinetic equations a set of macroscopic equations consistent with thermodynamic laws. Here we present a brief summary of the results in order to define notations and give the reader a better feel of the theory employed.

A. Irreversible thermodynamics of nonlinear processes

From the thermodynamic standpoint the entropy of a system is the most important quantity from which other thermodynamic functions and potentials are derived. In the phenomenological approach, we write the balance equation for entropy, treating it as if it is a matter. Thus, if we denote the entropy density by $\mathcal{S}$, the entropy flux by $\mathbf{J}_s$, and the entropy production by σ, then the entropy balance equation in the substantial derivative form is

$$\rho \frac{d\mathcal{S}}{dt} = -\operatorname{div} \mathbf{J}_s(\mathbf{r}, t) + \sigma(\mathbf{r}, t), \tag{2.1}$$

where ρ is the density of matter which depends on the position $\mathbf{r}$ and time t. Note that the entropy production σ is the source term and must be positive in compliance with the second law of thermodynamics. As it stands, Eq. (2.1) is incomplete as a partial differential equation for entropy density $\mathcal{S}$, since the entropy flux and the entropy production are not as yet known in terms of $\mathcal{S}$ and perhaps its derivatives. It is one of the major tasks in irreversible thermodynamics to find such relations and solve the differential equation. It is possible to gain an enormous amount of insight by studying Eq. (2.1) by means of kinetic equations appropriate for systems of interest. In fact, what we discuss in this paper is firmly rooted in kinetic theory,[7] although we make no further reference to it in the subsequent analysis made in this paper.

If an external electric field is present, the extended Gibbs relation may be cast, after a slight change in variables, in a more convenient form

$$T d\mathcal{S} = d\hat{\mathcal{E}} + p d\nu - z d\varphi_e - \sum_i \hat{\mu}_{ei}\, dc_i + \sum_{i\alpha} X_i^{(\alpha)} \odot d\hat{\Phi}_i^{(\alpha)}, \tag{2.2}$$

where φ_e is the potential, i.e.,

$$\begin{aligned} &\mathbf{E} = -\operatorname{grad} \varphi_e, \\ &\hat{\mathcal{E}} = \mathcal{E} + \sum_i z_i \varphi_e, \\ &\hat{\mu}_{ei} = \hat{\mu}_i + z_i \varphi_e, \\ &z = \sum_i c_i z_i, \end{aligned} \tag{2.3}$$

and $z_i = e_i/m_i$, e_i denoting the charge number of i and m_i its mass.

The conserved variables $\mathbf{u}$, ρ, and $\mathcal{E}$ satisfy the conservation laws which may be expressed as follows:

$$\frac{d\rho}{dt} = -\rho \operatorname{div} \mathbf{u}, \tag{2.4a}$$

$$\rho \frac{d}{dt} c_i = -\operatorname{div} \mathbf{J}_i + \mathcal{R}_i, \tag{2.4b}$$

$$\rho \frac{d}{dt} \mathbf{u} = -\operatorname{div} \mathbf{P} + \rho z \mathbf{E}, \tag{2.4c}$$

$$\rho \frac{d}{dt} \mathscr{E} = -\operatorname{div} \mathbf{Q} - \mathbf{P}:\operatorname{Grad} \mathbf{u} + \mathbf{J}_e \cdot \mathbf{E}, \tag{2.4d}$$

where $\mathscr{R}_i$ denotes the reaction rate and accounts for creation or destruction of species i due to "chemical reactions," and

$$\mathbf{P} = \sum_i \mathbf{P}_i \quad (\mathbf{P}_i = \text{stress tensor of } i),$$

$$\mathbf{Q} = \sum_i \mathbf{Q}_i \quad (\mathbf{Q}_i = \text{heat flux of } i),$$

$$\mathbf{J}_e = \sum_{i=1}^{r-1} z_i \mathbf{J}_i \quad (\mathbf{J}_i = \text{mass flux of } i).$$

Here we assume that there are $r-1$ charged species. In addition to the conservation laws which contain various fluxes, there are evolution equations for the fluxes

$$\Phi_i^{(\alpha)} = \rho \hat{\Phi}_i^{(\alpha)} \quad (i = 1,2,..,r;\ \alpha = 1,2,..., l),$$

where

$$\begin{aligned} \Phi_i^{(1)} &= [\mathbf{P}_i]^{(2)} = (\mathbf{P}_i + \mathbf{P}_i^t)/2 - (\mathbf{P}_i:\mathbf{U})\mathbf{U}/3, \\ \Phi_i^{(2)} &= (\mathbf{P}_i:\mathbf{U})/3 - p_i, \\ \Phi_i^{(3)} &= \mathbf{Q}_i - \hat{h}_i \mathbf{J}_i, \\ \Phi_i^{(4)} &= \mathbf{J}_i, \text{ etc.} \end{aligned} \tag{2.5}$$

with p_i denoting the hydrostatic pressure, $\hat{h}_i$ the enthalpy per unit mass of i, and $\mathbf{U}$ the unit second rank tensor. The evolution equations for fluxes may be written in the form

$$\rho \frac{d}{dt} \hat{\Phi}_i^{(\alpha)} = \hat{Z}_{ei}^{(\alpha)} + \Lambda_i^{(\alpha)} \quad (i = 1,2,...,r;\ = 1,2,..., l), \tag{2.6}$$

where $\hat{Z}_{ei}^{(\alpha)}$ is called the convective term and $\Lambda_i^{(\alpha)}$ the dissipative term. The former includes the convective current of $\hat{\Phi}_i^{(\alpha)}$ among various other terms, hence the name, and the dissipative term is generally a nonlinear function of $\hat{\Phi}_i^{(\alpha)}$. *It is the seat of irreversibility* as will be shown shortly. *The evolution equations (2.6) replace the constitutive relations appearing in other theories of irreversible thermodynamics.* In fact, if $\Lambda_i^{(\alpha)}$ is linearized with respect to $\hat{\Phi}_i^{(\alpha)}$ and only the thermodynamic forces such as the temperature gradients, concentration gradients, and velocity gradients are retained in the convective term, and if $d\hat{\Phi}_i/dt = 0$, then Eq. (2.6) is equivalent to the linear phenomenological relations in linear irreversible thermodynamics.

Since Eqs. (2.1) and (2.2) must be consistent with each other, we assume that the entropy flux consists of the usual classical expression given in terms of $\mathbf{Q}_i$, $\mathbf{J}_i$, and T and nonclassical contributions $\mathbf{J}_{sni}^{(\alpha)}$ as follows:

$$\mathbf{J}_s = \sum_i (\mathbf{Q}_i - \hat{\mu}_i \mathbf{J}_i)/T + \sum_{i\alpha} \mathbf{J}_{sni}^{(\alpha)}, \tag{2.7}$$

where $\mathbf{J}_{sni}^{(\alpha)}$ satisfy the equations

$$\operatorname{div} \mathbf{J}_{sni}^{(\alpha)} + T^{-1}[\hat{Z}_{ei}^{(\alpha)} \odot X_i^{(\alpha)} + \Phi_i^{(\alpha)} \odot \chi_i^{(\alpha)}] = 0. \tag{2.8}$$

Here various notations are

$$\chi_i^{(1)} = -[\operatorname{Grad} \mathbf{u}]^{(2)}, \tag{2.9a}$$

$$\chi_i^{(2)} = -\operatorname{div} \mathbf{u}, \tag{2.9b}$$

$$\chi_i^{(3)} = -\operatorname{grad} \ln T \tag{2.9c}$$

$$\chi_i^{(4)} = -\operatorname{grad}_T \hat{\mu}_i + (z_i - z)\mathbf{E} + \nu \operatorname{grad} p. \tag{2.9d}$$

Then Eqs. (2.1) and (2.2) are completely equivalent to each other, provided that the entropy production is given by Eq. (1.2). We call Eq. (2.8) the consistency conditions. Clearly, $\chi_i^{(\alpha)}$ as defined in Eq. (2.9) are linear irreversible thermodynamic forces. The fluxes $\mathbf{J}_{sni}^{(\alpha)}$ in the entropy flux are nonclassical and do not appear in linear irreversible thermodynamics. The above set (2.2)–(2.9) and Eq. (1.2) constitutes a coherent mathematical structure for irreversible thermodynamics for nonlinear processes.

B. Phenomenological model for carrier mobility

Precise forms for the evolution equations (2.6) may be obtained from the kinetic equation for the system, but they require calculations of collision integrals, which are not generally solved. The lack of precise knowledge of various scattering cross sections for processes in solids also reduces the feasibility of such molecular calculations. However, the flux dependence of the dissipative terms $\Lambda_i^{(\alpha)}$ is independent of the forms for the collision integrals involved. Therefore, by treating the collision integrals in the evolution equations as phenomenological parameters and fashioning the evolution equations in forms deemed useful for some phenomena in certain types of semiconductors, we hope to bridge the gap between the phenomenology and the microscopic theories of the phenomena. Here our main aim is to correlate some characteristic features of $\Lambda_i^{(\alpha)}$, and thus of the entropy production, with some distinctive experimental features which would eventually enable us to infer the structure of the entropy production from experimental data on various transport processes in semiconductors.

Let us take a semiconductor, e.g., GaAs. The currently accepted model for conductivity in such semiconductors assumes several valleys in the conduction band which have different effective masses for electrons. These conduction electrons collide with the lattice or phonons and thereby make transitions within the same valley or into another valley, changing their mobilities in the processes. There are also possibilities for two electrons in the same or different valleys to collide with each other and thereby for one electron to make a transition into the valley of the other electron. One might view these transitions as "chemical reactions"

$$e_1 \pm \hbar\omega_s \rightleftharpoons e_2, \tag{M}$$

$$e_1 + e_2 \rightleftharpoons 2e_1 \rightleftharpoons 2e_2 \tag{M'}$$

in which electron e_1 in valley 1 with effective mass m_1^* changes, either on absorption or emission of a phonon of frequency ω_s or on collision with electron e_2 in valley 2 with effective mass m_2^*, into either e_2 or e_1. Here for simplicity of analysis we shall assume that there is only one central and one satellite valley. Therefore, there are only two electron species to consider. As a further simplification we shall assume that there are no velocity gradients or temperature gradients, so that it is not necessary to consider stress and heat phenomena, but only the mass fluxes. Since the external field effect is generally dominant, we may neglect the concentration gradient in comparison with the field term in $\chi_i^{(4)}$. That is,

$$\chi_i^{(4)} \simeq (z_i - z)\mathbf{E} = z_i \mathbf{E} \quad (i = 1,2), \tag{2.10}$$

since $z = 0$ under the assumption. This is equivalent to an assumption that the charge neutrality holds locally. It is called the quasineutrality assumption.

The precise mathematical structures of the dissipative terms are poorly known, but there are some approximate forms known at present. In any case, the approximate forms for $\Lambda_i^{(\alpha)}$ must be subject to some constraints, the most important of which is the positivity condition. That is, $\Lambda_i^{(\alpha)}$ must be such that

$$\sum_{i\alpha} X_i^{(\alpha)} \odot \Lambda_i^{(\alpha)} \geqslant 0$$

in order to satisfy the local form of the second law of thermodynamics. Another requirement is that $\Lambda_i^{(\alpha)}$ must yield correct linear and nonlinear transport properties in agreement with experiment, since the evolution equations replace the constitutive relations between the fluxes and thermodynamic forces in the present approach.

The mechanisms (M) and (M′) suggest that the corresponding Boltzmann collision operators, and as a consequence the dissipative terms $\Lambda_i^{(\alpha)}$, are generally nonlinear with respect to the distribution functions. Since the distribution functions in practice must be expanded in a series of the fluxes in the system, the dissipative terms are also series in fluxes. Unfortunately, these series for $\Lambda_i^{(\alpha)}$—when truncated and truncate it we must in practice—give rise to an entropy production which is not necessarily positive for all allowed values of fluxes. This is tantamount to violating the second law of thermodynamics and the transport properties calculated with such dissipative terms do not generally meet the requirements by the second law. A simple-minded truncation of the series also has other undesirable consequences for the transport properties for nonlinear processes, such as an incorrect thermodynamic force dependence and wrong limiting laws. In order to remove such inadequacies of the series for the distribution functions and for the dissipative terms, a cumulant expansion method was devised, which guarantees the dissipative terms to be nonlinear with respect to the fluxes, as required for describing nonlinear transport processes, and at the same time to satisfy the positivity requirement by the second law. It turns out that the first and third order cumulant approximations yield an entropy production positive everywhere in the flux space. The first order cumulant approximation yields a monotonic entropy production and the transport coefficients calculated therewith, although correct, display nothing particular except that they are nonlinear with respect to the thermodynamic forces.

However, the third order cumulant approximation presents a qualitatively different situation. The dissipative terms to the third order cumulant approximation may be written in the form

$$\Lambda_i^{(\alpha)} = \sum_{j\beta} R_{ij}^{(\alpha\beta)} X_j^{(\beta)} \sinh(\bar{\kappa}/\kappa)/\kappa,$$

where $R_{ij}^{(\alpha\beta)}$ are coefficients made up of collision integrals, κ and $\bar{\kappa}$ are, respectively, a quadratic and quartic function of $X_i^{(\alpha)}$, and $X_i^{(\alpha)}$ are approximately proportional to $\mathbf{J}_i$ (see below). For vectorial processes such as diffusion and heat flow, it is not difficult to calculate formally the X dependence[8] of $\bar{\kappa}$, although the numerical values of the coefficients in $\bar{\kappa}$ are not easy to obtain because of the difficulty associated with getting the collision cross sections. What we have gained from such a formal calculation[8] of $\bar{\kappa}$ is a notion that $\bar{\kappa}$ can be nonmonotonic and the entropy production in that case becomes nonmonotonic in the flux space. This feature is something not seen in linear irreversible thermodynamics. It appears to have some important meanings for irreversible thermodynamics for systems removed far from equilibrium, and we would like to uncover them by means of specific examples. Since the geometric features of the entropy production surface probably are of importance, but not the mathematical form for σ, it may be convenient for analysis of macroscopic dynamics involved to devise simpler forms for σ and $\Lambda_i^{(\alpha)}$.

Under some favorable situations where the coefficients in $\bar{\kappa}$ have certain relations, $\bar{\kappa}/\kappa$ may be reduced to a quadratic form. When the hyperbolic sine function in the dissipative term given above is expanded and only the leading term is retained, the geometric feature of the corresponding entropy production remains roughly the same as that of the full function. This therefore motivates us to approximate the dissipative term with such a truncated expansion. When the terms in the approximate dissipative term are suitably rearranged to make the linear transport property more apparent, the resulting dissipative terms may be made to take the form as in Eq. (2.12) below.

When the assumption of no stress phenomena and heat flow is taken into account and when the approximation (2.10) is made use of, the convective term $\hat{Z}_{ei}^{(4)}$ may be written as

$$\hat{Z}_{ei}^{(4)} = \rho_i(z_i - z)\mathbf{E} = \rho_i z_i \mathbf{E}, \tag{2.11}$$

and we postulate the dissipative terms in the form

$$\Lambda_i^{(4)} = -\hat{L}_{ii}\hat{J}_i - \hat{L}_{ij}\hat{J}_j - \hat{N}_i\hat{J}_i(\lambda_1\hat{J}_1 + \lambda_2\hat{J}_2 - q_i)^2, \tag{2.12}$$

where $i \neq j = 1,2$. The coefficients $\hat{L}_{ii}$, $\hat{L}_{ij}$, $\hat{N}_i$, λ_i, and q_i are quantities independent of the fluxes. We stress that despite the motivations and approximations described above, the dissipative terms presented must be taken as phenomenological ones whose ultimate justification must be sought after in their ability to explain the experimental facts.

The coefficients $\hat{L}_{ij}$ are linear phenomenological coefficients satisfying the Onsager reciprocal relations[5,6]

$$\hat{L}_{ij} = \hat{L}_{ji} \tag{2.12′}$$

and $\hat{N}_i$, λ_i, and q_i are nonlinear phenomenological coefficients. They all depend on the field strength $E = |\mathbf{E}|$. In writing Eq. (2.12), we have made the approximation

$$X_i^{(4)} = -\hat{J}_i/c_i.$$

The last term in Eq. (2.12) reflects a nonlinear coupling between two mass fluxes due to the collisions of electrons in different valleys in the conduction band.

The evolution equations then take the forms

$$\rho\frac{d}{dt}\hat{J}_i = \rho_1 z_1\mathbf{E} - \hat{L}_{11}\hat{J}_1 - \hat{L}_{12}\hat{J}_2 - \hat{N}_1\hat{J}_1(\lambda_1\hat{J}_1 + \lambda_2\hat{J}_2 - q_1)^2, \tag{2.13}$$

$$\rho \frac{d}{dt}\hat{J}_2 = \rho_2 z_2 \mathbf{E} - \hat{L}_{21}\hat{J}_1 - \hat{L}_{22}\hat{J}_2 - \hat{N}_2\hat{J}_2(\lambda_1\hat{J}_1 + \lambda_2\hat{J}_2 - q_2)^2.$$

If we assume that the mass fluxes do not depend on the position vector $\mathbf{r}$, then the substantial derivative

$$(d/dt) = \mathbf{u}\cdot\nabla + (\partial/\partial t)$$

becomes the total time derivative, and Eq. (2.13) a set of ordinary differential equations. We write them as follows:

$$\begin{aligned}\frac{d}{dt}\hat{J}_1 &= c_1 z_1 \mathbf{E} - L_{11}\hat{J}_1 - L_{12}\hat{J}_2 - N_1\hat{J}_1(\lambda_1\hat{J}_1 + \lambda_2\hat{J}_2 - q_1)^2,\\ \frac{d}{dt}\hat{J}_2 &= c_2 z_2 \mathbf{E} - L_{21}\hat{J}_1 - L_{22}\hat{J}_2 - N_2\hat{J}_2(\lambda_1\hat{J}_1 + \lambda_2\hat{J}_2 - q_2)^2,\end{aligned} \tag{2.14}$$

where

$$L_{ij} = \rho^{-1}\hat{L}_{ij},$$
$$N_i = \rho^{-1}\hat{N}_i.$$

These are the equations we propose to study here. They appear to explain the main experimental features of the current–voltage characteristic exhibiting a negative differential mobility and associated noisy current fluctuation phenomena in semiconductors.

Equation (2.13) or Eq. (2.14) implies the entropy production in the form

$$\sigma = \rho T^{-1}[L_{11}\hat{J}_1^2 + L_{22}\hat{J}_2^2 + (L_{12}+L_{21})\hat{J}_1\hat{J}_2 + N_1\hat{J}_1^2(\lambda_1\hat{J}_1 + \lambda_2\hat{J}_2 - q_1)^2 + N_2\hat{J}_2^2(\lambda_1\hat{J}_1 + \lambda_2\hat{J}_2 - q_2)^2], \tag{2.15}$$

which is positive for all values of $\hat{J}_i$ if $N_i > 0$, $1 = 1,2$, and the linear phenomenological coefficients are such that

$$L_{11}, L_{22} > 0, \quad \begin{vmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{vmatrix} > 0. \tag{2.16}$$

See Fig. 1 for the entropy production surface. It is a nonmonotonic surface. Therefore, under the abovementioned conditions the transport processes described by Eq. (2.14) are assured to satisfy the second law of thermodynamics.

To study the set of equations (2.14), we first set[10]

$$\hat{\mathbf{J}}_1 = c_1 z_1 x(E)\mathbf{E}, \quad \hat{\mathbf{J}}_2 = c_2 z_2 y(E)\mathbf{E}, \tag{2.17}$$

where $x(E)$ and $y(E)$ are nonlinear mobilities which depend on the field strength $E = (\mathbf{E}\cdot\mathbf{E})^{1/2}$. In effect, these equations define the nonlinear mobilities, since they may be determined by solving the evolution equations (2.14).

In order to facilitate the solution of Eq. (2.14), we assume that c_k, $k = 1,2$, and $\mathbf{E}$ do not change in time and space over the span of time and distance in which the fluxes $\hat{J}_1$ and $\hat{J}_2$ change. This is equivalent to the assumption that there exists a separation of time scales in which the conserved variables and the external variables on one hand, and the fluxes on the other, change as the system evolves towards equilibrium. Therefore, the evolution equations are solved with the conserved variables in them kept fixed over the time span and space in which the fluxes evolve.

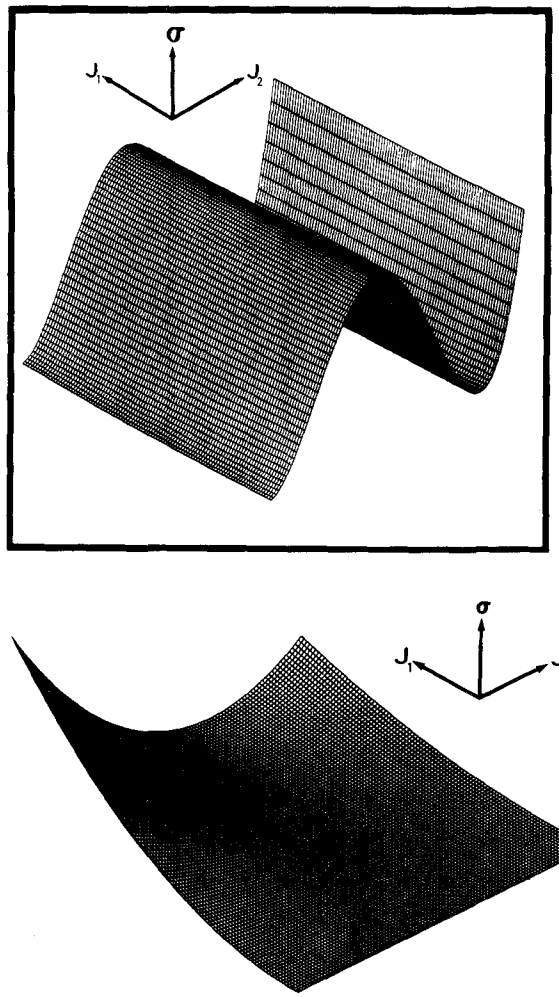

FIG. 1. (a) Entropy production surface (fine scale). The entropy production is nonmonotonic along the direction of J_2 and thus there exists another state besides the equilibrium state where the entropy production is minimum. (b) Entropy production surface (coarse scale). Since the entropy production for large J's is emphasized in this drawing, the fold structure in Fig. 1(a) is not apparent, being suppressed by the large J entropy production.

When Eq. (2.17) is used, the evolution equations finally take the following forms more suitable for study:

$$\begin{aligned}\frac{dx}{dt} &= 1 - \mathscr{L}_{11}x - \mathscr{L}_{12}y - N_1\alpha x\left(\frac{x}{x_g} + \frac{y}{y_g} - C\right)^2,\\ \frac{dy}{dt} &= 1 - \mathscr{L}_{21}x - \mathscr{L}_{22}y - N_2\alpha y\left(\frac{x}{x_g} + \frac{y}{y_g} - C\right)^2,\end{aligned} \tag{2.18}$$

where

$$\mathscr{L}_{ij} = L_{ij}Z_{ji}, \quad \mathscr{L}_{11} = L_{11}, \quad \mathscr{L}_{22} = L_{22}, \tag{2.19}$$

$$Z_{12} = \rho_1 z_1/\rho_2 z_2 = 1/Z_{21}, \quad c = q_1/E = q_2/E,$$
$$x_g = 1/c_1 z_1 \lambda_1, \quad y_g = 1/c_2 z_2 \lambda_2, \quad \alpha = E^2. \tag{2.20}$$

The solution to this set of equations x and y yields the current $\mathbf{J}_e$:

$$\mathbf{J}_e = \rho(z_1\hat{J}_1 + z_2\hat{J}_2) = (\rho_1 z_1^2 x + \rho_2 z_2^2 y)\mathbf{E}. \tag{2.21}$$

Before we study Eq. (2.18) for some particular cases in the next section, we discuss the significance of the linear pheno-

menological coefficients in Eq. (2.18) in more detail.

If α is sufficiently small, then the nonlinear terms in Eq. (2.18) may be ignored in comparison with the linear terms which do not depend on α. We thus obtain

$$\frac{dx}{dt} = 1 - \mathscr{L}_{11}x - \mathscr{L}_{12}y,$$
$$\frac{dy}{dt} = 1 - \mathscr{L}_{21}x - \mathscr{L}_{22}y. \tag{2.22}$$

The steady state solution to these equations is stable when the conditions on the coefficients as in Eq. (2.16) are satisfied, and yields linear phenomenological mobilities:

$$x_0 = \frac{\mathscr{L}_{22} - \mathscr{L}_{12}}{\mathscr{L}_{11}\mathscr{L}_{22} - \mathscr{L}_{12}\mathscr{L}_{21}},$$
$$y_0 = \frac{\mathscr{L}_{11} - \mathscr{L}_{21}}{\mathscr{L}_{11}\mathscr{L}_{22} - \mathscr{L}_{12}\mathscr{L}_{21}}. \tag{2.23}$$

Since the stability of the steady state of Eq. (2.22) implies that the time-dependent solution to Eq. (2.22) approaches the steady state asymptotically in time, the asymptotic solution to Eq. (2.22) implies Ohm's law in terms of the steady state solution:

$$\mathbf{J}_e = (\mu_{01} + \mu_{02})\mathbf{E} = \mu_0\mathbf{E}, \tag{2.24}$$

where

$$\mu_{0k} = \frac{\rho_k z_k^2(\mathscr{L}_{ll} - \mathscr{L}_{kl})}{\mathscr{L}_{11}\mathscr{L}_{22} - \mathscr{L}_{12}\mathscr{L}_{21}} \quad (k \neq l = 1,2).$$

Therefore, the phenomenological coefficients $\mathscr{L}_{kl}(k \neq l = 1,2)$ may be deduced from the data on the current at the low field region where Ohm's law holds.

III. THE STEADY STATES OF THE EVOLUTION EQUATIONS

There still are parameters N_i and λ_i, $i = 1,2$, which are not yet fully specified. They are taken as phenomenological parameters as are the linear coefficients. Since the situation does not seem simple, a systematic investigation appears essential and some analytic results, if possible, would be very helpful. The parameters λ_i will be chosen with such results in mind. Based on the examinations made with the parameters chosen, we then will be able to suggest an explanation for the observation made by Kabashima *et al.*[1] on GaAs. Since we require a linear stability analysis, we begin with it.

A. Linear stability analysis: Preliminary

Let us denote a steady state of Eq. (2.18) by (x_s, y_s). Then it is a root of the equations

$$1 - \mathscr{L}_{11}x_s - \mathscr{L}_{12}y_s - \alpha N_1 x_s\left(\frac{x_s}{x_g} + \frac{y_s}{y_g} - C\right)^2 = 0,$$
$$1 - \mathscr{L}_{21}x_s - \mathscr{L}_{22}y_s - \alpha N_2 y_s\left(\frac{x_s}{x_g} + \frac{y_s}{y_g} - C\right)^2 = 0. \tag{3.1}$$

In order to simplify the equations involved, it is convenient to define the following notations:

$$S = \frac{x_s}{x_g} + \frac{y_s}{y_g} - C, \quad p_1 = S^2 + 2Sx_2/x_g,$$
$$p_2 = S^2 + 2Sy_s/y_g. \tag{3.2}$$

With new variables u_1 and u_2 defined by

$$x = x_s + u_1, \quad y = y_s + u_2, \tag{3.3}$$

Eq. (2.16) may be recast into a form more suitable for stability analysis:

$$\frac{d}{dt}\mathbf{u} = -\Lambda\mathbf{u} - \alpha\mathbf{Q}(u_1, u_2), \tag{3.4}$$

where

$$\mathbf{u} = \{u_1, u_2\}, \tag{3.5a}$$
$$\Lambda = \begin{pmatrix} \Lambda_{11} & \Lambda_{12} \\ \Lambda_{21} & \Lambda_{22} \end{pmatrix}, \tag{3.5b}$$
$$\Lambda_{11} = \mathscr{L}_{11} + \alpha N_1 p_1, \quad \Lambda_{22} = \mathscr{L}_{22} + \alpha N_2 p_2, \tag{3.5c}$$
$$\Lambda_{12} = \mathscr{L}_{12} + 2\alpha N_1 Sx_s/y_g,$$
$$\Lambda_{21} = \mathscr{L}_{21} + 2\alpha N_2 Sy_s/x_g,$$
$$\mathbf{Q} = \{Q_1, Q_2\}, \tag{3.5d}$$
$$Q_1 = N_1\left[(x_s + u_1)\left(\frac{u_1}{x_g} + \frac{u_2}{y_g}\right)^2 + 2u_1 S\left(\frac{u_1}{x_g} + \frac{u_2}{y_g}\right)\right], \tag{3.5e}$$
$$Q_2 = N_2\left[(y_s + u_2)\left(\frac{u_1}{x_g} + \frac{u_2}{y_g}\right)^2 + 2u_2 S\left(\frac{u_1}{x_g} + \frac{u_2}{y_g}\right)\right]. \tag{3.5f}$$

The linear stability analysis of Eq. (3.4) amounts to finding the eigenvalues of the matrix Λ. They are given by the formula

$$\omega^{(\pm)} = \tfrac{1}{2}(\Lambda_{11} + \Lambda_{22}) \pm \tfrac{1}{2}[(\Lambda_{11} - \Lambda_{22})^2 + 4\Lambda_{12}\Lambda_{21}]^{1/2}. \tag{3.6}$$

These eigenvalues will be examined for their signs when the steady states are found.

The evolution equation will acquire more useful forms if we define the parameters λ_i, $i = 1,2$, e.g., x_g and y_g in the following forms:

$$x_g = \frac{\mathscr{L}_{22} + \alpha N_2(C-2)^2 - \mathscr{L}_{12}}{[\mathscr{L}_{11} + \alpha N_1(C-2)^2][\mathscr{L}_{22} + \alpha N_2(C-2)^2] - \mathscr{L}_{12}\mathscr{L}_{21}},$$
$$y_g = \frac{\mathscr{L}_{11} + \alpha N_1(C-2)^2 - \mathscr{L}_{21}}{[\mathscr{L}_{11} + \alpha N_1(C-2)^2][\mathscr{L}_{22} + \alpha N_2(C-2)^2] - \mathscr{L}_{12}\mathscr{L}_{21}}. \tag{3.7}$$

It is easy to verify that this set (x_g, y_g) is a steady state of the evolution equations (2.18). With this choice of the parameters, the nonlinear terms of the evolution equations are scaled by one of the steady states of the equations them-

selves. We will call this steady state the primary branch of steady states. It will turn out to be that this steady state is the only one which is physical in the low field region and yields the current–voltage relation reducing to the Ohmic law. The parameters N_i, $i = 1,2$, will be simply regarded as constants indicating the strengths of the nonlinear couplings.

B. Steady states

There can be steady states other than the primary branch. In order to find them, we must solve Eq. (3.1) for (x_s, y_s). Physically transparent analytic solutions are not possible to obtain unless we assume a particular set of parameter relations as will be done later. But before we take that approach, it is useful to develop a graphical method which gives deeper insights into the problem. It would also guide us in choosing physically meaningful parameters for the equations.

Solution of Eq. (3.1) is facilitated if we make the transformations

$$x_s = x_g + v_1, \quad y_s = y_g + v_2, \tag{3.8}$$

and

$$R = \frac{1}{2}\left(\frac{v_1}{x_g} + \frac{v_2}{y_g}\right), \quad r = \frac{1}{2}\left(\frac{v_1}{x_g} - \frac{v_2}{y_g}\right). \tag{3.9}$$

With the above transformations, Eq. (3.1) is transformed to a pair of algebraic equations

$$R = -\alpha A^{(+)}(1+R)M_R - \alpha B^{(+)} r M_R, \tag{3.10a}$$

$$r = -\alpha A^{(-)}(1+R)M_R - \alpha B^{(-)} r M_R, \tag{3.10b}$$

where

$$M_R = 4R^2 + 4(2-C)R, \tag{3.11}$$

$$A^{(\pm)} = \tfrac{1}{2}[N_1(d_{11} \pm \xi_{21} d_{21}) + N_2(\xi_{12} d_{12} \pm d_{22})], \tag{3.12a}$$

$$B^{(\pm)} = \tfrac{1}{2}[N_1(d_{11} \pm \xi_{21} d_{21}) - N_2(\xi_{12} d_{12} \pm d_{22})] \tag{3.12b}$$

with the definitions of the symbols as follows:

$$\xi_{12} = 1/\xi_{21} = y_g/x_g, \quad d_{11} = [\mathscr{L}_{11} + \alpha N_1(2-C)^2]/\Delta, \quad d_{12} = -\mathscr{L}_{12}/\Delta, \quad d_{21} = -\mathscr{L}_{21}/\Delta,$$
$$d_{22} = [\mathscr{L}_{22} + \alpha N_2(2-C)^2]/\Delta, \quad \Delta = [\mathscr{L}_{11} + \alpha N_1(2-C)^2][\mathscr{L}_{22} + \alpha N_2(2-C)^2] - \mathscr{L}_{12}\mathscr{L}_{21}. \tag{3.13}$$

Solving Eq. (3.10b) for r to obtain

$$r = -\frac{\alpha A^{(-)}(1+R)M_R}{1 + \alpha B^{(-)} M_R} \tag{3.14}$$

and substituting it into Eq. (3.10a), we obtain the equation for R,

$$R = -A^{(+)}(1+R)M_R + \frac{\alpha^2 A^{(-)} B^{(+)}(1+R)M_R^2}{1 + \alpha B^{(-)} M_R}. \tag{3.15}$$

The solution of this equation provides the steady states desired. It has a trivial solution

$$R = 0 \tag{3.16}$$

which implies

$$r = 0$$

and thus corresponds to (x_g, y_g), the primary steady state. Nontrivial solutions may be found as follows with a graphical method. It can be easily developed if we recast this equation by dividing it with $(1+R)M_R$ and rearranging the terms in the following form:

$$\frac{1}{(R+1)(R+2-C)} = -\epsilon\left[1 + \frac{\beta}{(R - \frac{1}{2}C + 1 + P_0)(R - \frac{1}{2}C + 1 - P_0)}\right], \tag{3.17}$$

where

$$\epsilon = 4\alpha(A^{(+)}B^{(-)} - A^{(-)}B^{(+)})/B^{(-)},$$
$$\beta = A^{(-)}B^{(+)}/4\alpha B^{(-)}(A^{(+)}B^{(-)} - A^{(-)}B^{(+)}), \tag{3.18}$$
$$\delta = 1/4\alpha B^{(-)}, \quad P_0 = \tfrac{1}{2}[(C-2)^2 - 4\delta]^{1/2}.$$

The transformation

$$R = \tfrac{1}{2}C - 1 + P \tag{3.19}$$

yields a neater equation

$$\frac{1}{(P + C' + 1)(P - C')} = -\epsilon\left[1 + \frac{\beta}{(P - C' + P_0)(P - C' - P_0)}\right], \tag{3.20}$$

where

$$C' = \tfrac{1}{2}C - 1.$$

The steady states are determined by the real roots of Eq. (3.20); namely, the intersections of the functions on the left and right-hand sides of Eq. (3.20). [We note that Eq. (3.20), of course, can be exactly solved. But the solutions are not transparent.] The left-hand side $f_L(P)$ has singularities at $P_{1,2} = C'$ and $-(C'+1)$, while the right-hand side $f_R(P)$ has singularities at $P_{3,4} = C' \pm P_0$. If the parameters are such that

$$(C-2)^2 - 4\delta > 0, \tag{3.21}$$

and P_3 and P_4 are real, but if

$$(C-2)^2 - 4\delta < 0, \tag{3.22}$$

then P_3 and P_4 are complex. Depending on the conditions (3.21) and (3.22) on the discriminant and the signs of ϵ and β, the function $f_R(P)$ assumes different forms and the details of the root structures become different. But the general situation is that there is either one or two nontrivial roots or no root at all. Various different cases are summarized in Fig. 2, where the solid curves represent the three branches of $f_L(P)$ and the vertical broken lines the positions of the singularities, and the dotted curves represent the branches of the

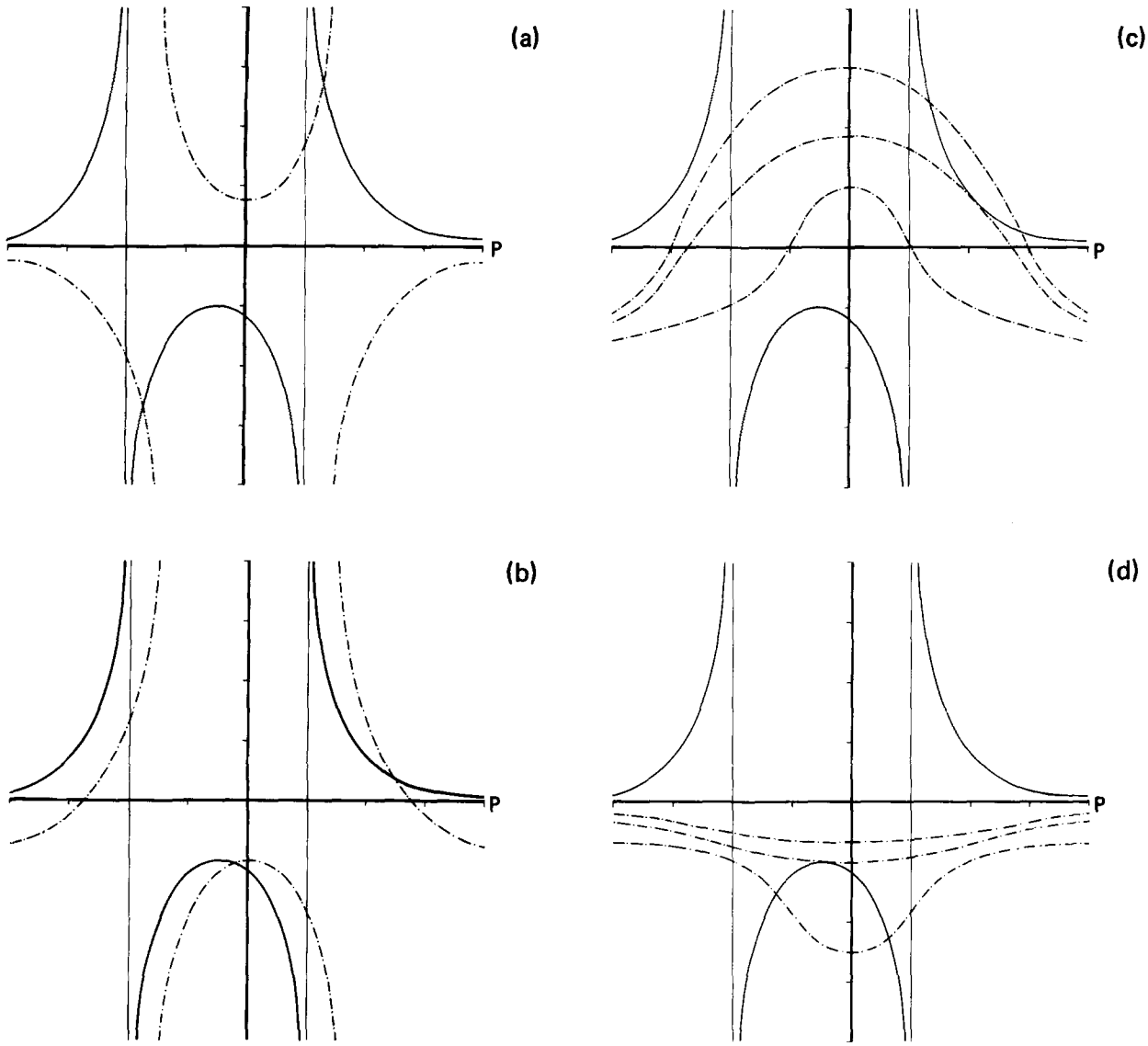

FIG. 2. (a)–(d) Root structures. The solid lines are f_L and the broken lines are f_R.

function $f_R(P)$. The branches of $f_R(P)$ move as α increases and, depending on the values of α and other parameters, one or more of the branches of $f_R(P)$ cross at least one branch of $f_L(P)$. Figure 3 represents the root structure corresponding to the assumptions on the relations between phenomenological coefficients below [Eqs. (4.1) and (4.2)], which yield simple analytic forms for the roots. Together with the stability analysis presented, this information on the root structure provides a useful means of understanding experimental data.

IV. MULTIPLE STEADY STATES AND CURRENT FLUCTUATIONS

To make the analysis more tractable and transparent, we will make the following assumptions on relations between phenomenological parameters:

$$\mathscr{L}_{11} = Z_{12}^2 \, \mathscr{L}_{22}, \tag{4.1}$$

$$N_1 = Z_{12}^2 \, N_2. \tag{4.2}$$

The first assumption is roughly equivalent to an assumption on the ratio of the linear mobilities of the two carrier species of different masses m_1^* and m_2^*. Since according to the kinetic theory the nonlinear parameters N_1 and N_2 are related to the transport (collision bracket) integrals for the nonlinear

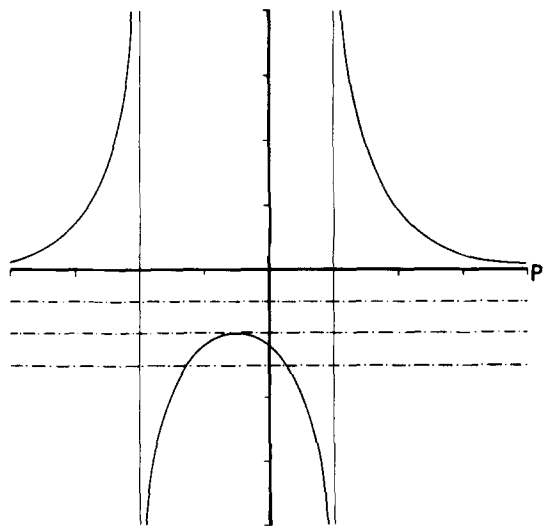

FIG. 3. Root structure in the case of assumptions (4.1) and (4.2). The meanings of the lines are the same as in Figs. 2(a)–(d).

terms, the second assumption is equivalent to an assertion that the collision bracket integrals for N_1 and N_2 scale according to Eq. (4.2). Since the integrals are structurally the same for both carrier species and the only differences between them are the masses and the populations of the two species, the assumption appears quite reasonable. The physical consequences of these assumptions will become evident as we proceed and will be pointed out.

Since the low-field linear conductivities are approximately

$$\mu_{10} \simeq \rho_1 z_1 / \mathscr{L}_{11}, \quad \mu_{20} \simeq \rho_2 z_2 / \mathscr{L}_{22}$$

if the couplings $\mathscr{L}_{12}$ and $\mathscr{L}_{21}$ are neglected, the assumption (4.1) is equivalent to the following relation between the conductivities:

$$\frac{\rho_1 \mu_{20}}{\rho_2 \mu_{10}} = 1. \tag{4.3}$$

Since the effective mass ratio[11] is

$$m_1^*/m_2^* = 0.36/0.072 = 5$$

and according to experiment

$$\frac{\mu_{20}}{\mu_{10}} = \frac{5200}{145} = 36,$$

the ratio (4.3) is fulfilled if the population ratio is

$$n_2/n_1 = 7,$$

where n_1 and n_2 are the populations of heavy and light mass species.

By using the relations (4.1) and (4.2) and the reciprocal relations $L_{12} = L_{21}$ [cf. Eq. (2.12′)], we obtain

$$y_g(\alpha) = Z_{12}^2 \, x_g(\alpha), \tag{4.4}$$

where $x_g(\alpha)$ now is given by a rather simplified formula

$$x_g(\alpha) = \frac{x_g(0)}{1 + \alpha N_1 \, x_g(0)(C-2)^2}, \tag{4.5}$$

$$x_g(0) = \frac{1}{\mathscr{L}_{11} + \mathscr{L}_{21}}. \tag{4.6}$$

Equation (4.6) is a special case of Eq. (2.23) and is related to the zero-field mobility of the heavier mass species. Besides these simplifications they have made possible, the assumptions (4.1) and (4.2) also give rise to tractable analytic forms, although somewhat restrictive, for other steady states which we need to make the analysis complete. They give rise to the identities

$$A^{(+)} = N_2(d_{22} + d_{21}), \quad A^{(-)} = 0, \quad B^{(+)} = 0, \quad B^{(-)} = N_2(d_{22} - d_{21}). \tag{4.7}$$

These identities yield

$$r = 0 \tag{4.8}$$

which implies

$$v_2(\alpha) = (y_g/x_g) v_1(\alpha) = Z_{12}^2 \, v_1(\alpha) \tag{4.9}$$

and

$$\beta = 0,$$

so that Eq. (3.20) becomes

$$\frac{1}{(P + C' + 1)(p - C')} = -\epsilon. \tag{4.10}$$

The root structures of this equation are given for different values of α in Fig. 3. There are three cases possible, depending on the value of α(or ϵ): (i) no real root; (ii) one real root; and (iii) two real roots. In general, after reverting back to the variable R, we find the roots in the forms

$$R^{(\pm)} = \tfrac{1}{2}(C-2) \pm \tfrac{1}{2}[(2C-3) - (C-2)^2 \alpha_m/\alpha]^{1/2}, \tag{4.11}$$

where

$$\alpha_m = \frac{\mathscr{L}_{11} + \mathscr{L}_{21}}{N_1(2-C)^2}, \tag{4.12}$$

which is the point of maximum in the current–voltage relation calculated with the (x_g, y_g) pair. The steady states corresponding to $R^{(\pm)}$ are

$$x_s^{(\pm)} = \tfrac{1}{2} x_g \{C - 1 \pm [2C - 3 - (C-2)^2 \alpha_m/\alpha]^{1/2}, \quad y_s^{(\pm)} = Z_{12}^2 \, x_s^{(\pm)}. \tag{4.13}$$

These steady states are complex and therefore unphysical when

$$\alpha < [(2-C)^2/(2C-3)]\alpha_m = \alpha_c. \tag{4.14}$$

The complex roots belong to the case of no real root mentioned above. The case of a single real root arises when the discriminant in Eq. (4.13) is equal to zero. The zero of the discriminant defines the critical field α_c. The case of two real roots corresponds to the value of α which makes the discriminant positive.

In summary of steady states, there are at most two steady states: (i) (x_g, y_g) where x_g and y_g are defined by Eq. (4.4) or Eq. (4.5) and Eq. (4.4) as a consequence of Eq. (4.1); and (ii) $(x_s^{(\pm)}, y_s^{(\pm)})$, where $x_s^{(\pm)}$ and $y_s^{(\pm)}$ are defined by Eq. (4.13). These steady states show up only in the region of α larger than the critical value α_c. Since α_c is generally larger than the values of α where Ohm's law holds, the multiple steady states appear beyond the Ohmic region and the system starts exhibiting a rather complex dynamical behavior as α increases beyond α_c. The trajectories of the steady states in the current–voltage plane are given in Fig. 4.

The trajectories cross each other as is evident in Fig. 4. We calculate the crossing point α_x. The crossing point is defined by the equation

$$x_s^{(\pm)}(\alpha_x) = x_g(\alpha_x).$$

Substituting Eq. (4.13) into this condition, we find

$$C - 3 = \mp [2C - 3 - (2-C)^2 \alpha_m/\alpha_x]^{1/2}. \tag{4.15}$$

If $C - 3 > 0$ which is the case of the present analysis, only the lower steady state branch $(x_s^{(-)}, y_s^{(-)})$ can cross the primary branch, and it does so at

$$\alpha_x = [(C-2)/(6-C)]\alpha_m. \tag{4.16}$$

This crossing point occurs at a point in α larger than α_c, i.e., $\alpha_x > \alpha_c$.

Now equipped with the analytic forms for the steady states, we are able to complete the stability analysis initiated in the previous subsection. The assumptions (4.1) and (4.2) give rise to the relations

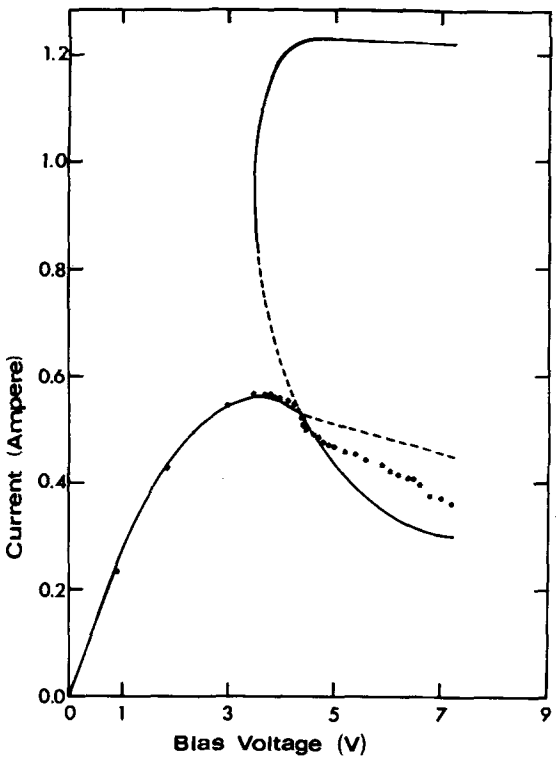

FIG. 4. The current–bias voltage relation. The solid lines are stable steady states and the broken lines are unstable steady states. The filled circles are the experimental data on GaAs. See Ref. 13 for the nature of the experimental data for $\alpha > \alpha_x$.

$$\Lambda_{11} = Z_{12}^2 \Lambda_{22}, \quad \Lambda_{21} = Z_{12}^2 \Lambda_{12}$$

which in turn yield the eigenvalues in the form

$$\omega^{(\pm)} = \tfrac{1}{2}(1 + Z_{12}^2)\Lambda_{22} \pm \tfrac{1}{2}[\Lambda_{22}^2(1 - Z_{12}^2) + 4Z_{12}^2 \Lambda_{12}^2]^{1/2}. \tag{4.17}$$

The stability of the steady states is determined by examining zeros of $\omega^{(\pm)}$.

A. Stability of (x_g, y_g)

It turns out that the zero of Eq. (4.17) occurs at α_x which is the crossing point of x_g with $x_s^{(-)}$. If $\alpha < \alpha_x$, then

$$\omega^{(\pm)} > 0,$$

and the steady state is stable, but if $\alpha > \alpha_x$, then

$$\omega^{(-)} \leqslant 0, \quad \omega^{(+)} > 0,$$

and the steady state loses its stability. Therefore, the crossing point α_x is a stability exchange point for the primary branch (x_g, y_g) and the lower branch $(x_s^{(-)}, y_s^{(-)})$, as will be shown shortly. Since the primary branch is stable in the region $0 \leqslant \alpha \leqslant \alpha_c (\alpha_c < \alpha_x)$ and there is only one steady state in the interval $0 \leqslant \alpha < \alpha_c$, the solution of the evolution equations (2.18) or (3.4) asymptotically approaches the primary branch (x_g, y_g) and consequently the long time current in the interval $0 \leqslant \alpha < \alpha_c$ is entirely determined by the primary branch itself. That is,

$$J_{e\infty}^{(0)} = \lim_{t\to\infty} J_e = \lim_{t\to\infty} [\rho_1 z_1^2 x(t) + \rho_2 z_2^2 y(t)]E = (\rho_1 z_1^2 x_g + \rho_2 z_2^2 y_g)E \tag{4.18}$$

for $0 \leqslant \alpha < \alpha_c$. This result is in accordance with the well-known theorem[12] on the asymptotic stability of a steady state.

B. Stability of $(x_s^{(-)}, y_s^{(-)})$

The lower branch $(x_s^{(-)}, y_s^{(-)})$ is found unstable in the interval $\alpha_c < \alpha < \alpha_x$, but becomes stable in the region $\alpha > \alpha_x$ where the primary branch is unstable as mentioned before. Again, the crossing point α_x is a stability exchange point when the lower branch becomes stable. Therefore according to the theorem on the asymptotic stability aforementioned the long time current can assume the value given by the asymptotic form

$$J_{e\infty}^{(-)} = \lim_{t\to\infty} J_e = (\rho_1 z_1^2 x_s^{(-)} + \rho_2 z_2^2 y_s^{(-)})E \tag{4.19}$$

in the region of $\alpha > \alpha_x$.

C. Stability of $(x_s^{(+)}, y_s^{(+)})$

Explicit calculation shows that the upper branch $(x_s^{(+)}, y_s^{(+)})$ is always stable in the region $\alpha \geqslant \alpha_c$ since both eigenvalues $\omega^{(\pm)}$ are positive there. Therefore the long time current may take the value given by the formula

$$J_e^{(+)} = \lim_{t\to\infty} J_e = (\rho_1 z_1^2 x_s^{(+)} + \rho_2 z_2^2 y_s^{(+)})E \tag{4.20}$$

for $\alpha \geqslant \alpha_c$.

These results of stability analysis for the three branches of steady state are summarized in Fig. 4 where the solid lines denote the stable portions of the steady states, while the dotted lines represent the unstable portions. The filled circles[13] are the experimental data on the current–voltage characteristic obtained by Kabashima *et al.*[1] for GaAs. In Table I are given the numerical values of the parameters corresponding to the steady states calculated. The current–voltage characteristic may be scanned in the following manner: As E increases from zero, the current increases in magnitude according to Ohm's law as predicted by the low field primary steady state (x_g, y_g) and, as E increases, a deviation from the Ohmic law becomes noticeable and the current passes through a maximum at $E_m = \sqrt{\alpha_m}$. As E reaches $E_c = \sqrt{\alpha_c}$, there appears a pair of steady states in addition to the primary branch, the upper one of the pair being stable and the lower one unstable. The primary branch still remains stable. As E further increases and crosses $E_x = \sqrt{\alpha_x}$, the primary branch and the lower secondary branch exchange their stability and we have a pair of stable steady states separated by an unstable primary steady state. Therefore, the situation at $E = E_x$ along the primary steady state branch appears exact-

TABLE I. Parameters.

$\mathscr{L}_{11}$	$6.74 \times 10^{-3}\ s^{-1}$
$\mathscr{L}_{22}$	$1.88 \times 10^{-4}\ s^{-1}$
$\mathscr{L}_{21}$	$1.56 \times 10^{-4}\ s^{-1}$
$\mathscr{L}_{12}$	$4.35 \times 10^{-6}\ s^{-1}$
Z_{12}	5.99
C	4.3209
N_1	$9.35 \times 10^{-5}\ cm^2/V^2\ s$
N_2	$2.61 \times 10^{-6}\ cm^2/V^2\ s$
n_2	$3.7 \times 10^{14}\ cm^{-3}$

ly like a pitchfork bifurcation[14] with one stable branch moving backward on the E axis. Although there is some numerical differences, the stable lower secondary branch $(x_s^{(-)}, y_s^{(-)})$ behaves in a qualitatively correct manner, when compared with the experimental data by Kabashima *et al.*[1] (see Ref. 13). Although it is not easy to achieve, a better choice of parameters may improve the fitting. Kabashima *et al.* also observed noisy fluctuations in the current beyond a certain critical value of E which is approximately equal to E_x. The fact that the unstable primary steady state branch is flanked by two stable secondary steady state branches in the region $E > E_x$ explains this fluctuation phenomenon, since depending on the initial condition the solution of the evolution equations (2.18) may evolve towards either $(x_s^{(+)}, y_s^{(+)})$ or $(x_s^{(-)}, y_s^{(-)})$, resulting in the value predicted by $J_{e\infty}^{(+)}$ or $J_{e\infty}^{(-)}$ for the current. This is borne out by actual numerical solutions of Eq. (2.18) and is illustrated in Fig. 5 showing trajectories in the xy-phase plane. If the initial condition (x_i, y_i) is such that $(x_i + y_i) < (x_g + y_g)$, then

$$(x, y) \to (x_s^{(-)}, y_s^{(-)}),$$

whereas if (x_i, y_i) is such that

$$(x_i + y_i) > (x_g + y_g),$$

then

$$(x, y) \to (x_s^{(+)}, y_s^{(+)})$$

as $t \to \infty$. Since the initial conditions must be given by a certain distribution, e.g., a random distribution, the above-mentioned behavior of the solution seems to account for the noisy fluctuations in the current observed in experiment.[1] (It is also important to recall how the experiment is done.[13]) Therefore, we suggest that *the presence of multiple steady states—one unstable flanked by two stable steady states—may be at the root of the fluctuation phenomenon* observed by Kabashima *et al.* in the region of $E > E_x$. The fluctuating currents in GaAs were attributed to oscillations[15] in the local field or explained away with a fluctuation theory.[16] The local field oscillation theory assumes phenomenological current-field characteristic which exhibits a negative differential mobility in the high field region and a linear relation between J_e and E. These features are quite different from the present theory. The fluctuation theory does not explain why we see what is observed in experiment except that it stems from fluctuations due to as yet unknown causes. We see through the present study that small fluctuations in the initial conditions tend to get amplified through nonlinear couplings which give rise to a bifurcation of steady states into stable high and low current states and consequently cause the system wander between the two stable steady states as α crosses the critical value α_x. This explanation is basically different from those offered in Refs. 15 and 16.

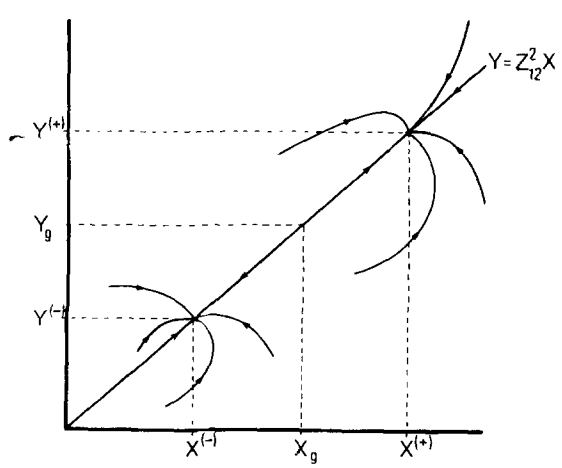

FIG. 5. Trajectories in the (x, y) phase plane (a qualitative sketch based on numerical solutions). The line $y = Z_{12}^2\, x$ is the locus of the steady states.

V. DISCUSSION AND CONCLUSION

The evolution equations presented in this paper are so constructed as to be consistent with the second law of thermodynamics, since they give rise to a positive entropy production. It is nonmonotonic as a function of the mass fluxes. This is a significant departure from the entropy production in linear irreversible thermodynamics. We believe that this difference is worth noting, since it is intimately tied up with the complex dynamical behavior of the solutions which we have observed to stem from the nonlinearity and ultimately the nonmonotonic entropy production. It must be stressed that the possibility of nonlinear dynamics does not exist in the case of monotonic quadratic entropy productions which we see in linear irreversible thermodynamics. We believe that nonmonotonic entropy productions[17] play an important role in formulating macroscopic theories of nonlinear transport processes and nonlinear dynamics related to macroscopic processes in general. Being nonlinear, the evolution equations have the properties and features typical of nonlinear systems of ordinary differential equations. We have seen that the evolution equations (2.18) can have three steady states and thus we have here a physically realistic example of multiple steady state system which is rooted in a kinetic theory of many-body systems, e.g., the Boltzmann equation and its generalization. With a pair of assumptions on relations between phenomenological coefficients, we have explicitly shown that the emergence of multiple steady states may be responsible for the current fluctuations observed in GaAs by Kabashima *et al.* Removal of the assumptions would not alter the interpretation we offer here for the experimental observation, since the graphical method presented demonstrates that the number of steady states and their geometric relationship remain unchanged, although their precise values would change. Since the qualitatively same mathematical structure of steady states is what is required for the invariance of the qualitative aspects of the theoretical results under a change of parameters, the graphical method fortifies the above assertion.

During our investigation of numerical solutions of Eq. (2.18), we have encountered transient oscillatory solutions which spiral out of the primary steady state that has just turned unstable, if a certain set of parameters is chosen. For the interested reader we present an example of such solutions in Fig. 6, which shows a spiral issuing from an initial state near the unstable primary steady state branch. It is an example of the richness of features the evolution equations postulated here possess.

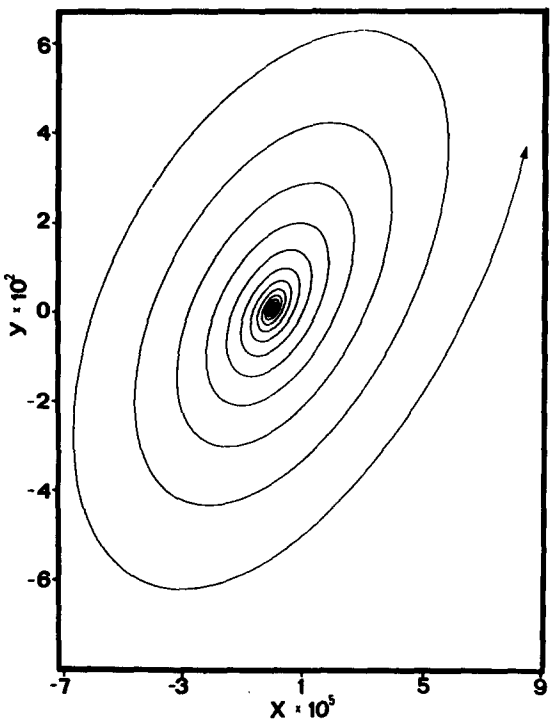

FIG. 6. A transient oscillatory (spiral) solution issuing from an unstable primary branch (x_g, y_g). The solution eventually goes to stable steady state $(x_s^{(+)}, y_s^{(+)})$.

The concept of availability originally put forth by Keenan[18] is recently revived by Salamon and Berry[19] to extend thermodynamics to nonequilibrium states. According to the original concept, the availability is related to the inherent irreversibility through the loss of available work. Thus the dissipated availability is related to the entropy production. Therefore, it might seem plausible to replace the entropy production with the dissipated availability, and formulate a theory of irreversible processes with the latter. It seems clear, however, that whatever is introduced to replace the entropy production must meet the second law requirement and its precise physical and mathematical content must also be made explicit in order to carry out a formulation of a theory of irreversible thermodynamics. Salamon and Berry show that the dissipated availability ΔA_u may be given in terms of a bilinear form of internal energy derivatives with respect to extensive variables and the time derivatives of the latter, if the internal energy is a function of the extensive variables chosen

$$\Delta A_u = \int_0^\tau dt \sum_i \left[(\partial \mathscr{E}/\partial W_i)_{\text{equil}} - (\partial \mathscr{E}/\partial W_i)\right](dW_i/dt), \tag{5.1}$$

where W_i are the extensive variables and $\mathscr{E}$ is the internal energy

$$\mathscr{E} = E(W_1, W_2, \ldots, W_n).$$

This form for the dissipated availability, however, is not the same as the entropy production used in the present and previous papers.[7-9] The difference is easy to see. In the present theory the entropy production (1.2) may be written in the form

$$\sigma = \sum_{i\alpha} (\partial \mathscr{S}/\partial \hat{\Phi}_i^{(\alpha)}) \odot \Lambda_i^{(\alpha)}, \tag{5.2}$$

if the extended Gibbs relation (1.1) is employed to calculate $X_i^{(\alpha)}$. If this is integrated over a time span, say, from 0 to τ, then we find the total entropy production produced in the unit volume of the system around the position r is

$$\sigma_{\text{total}} = \int_0^\tau dt \sum_{i\alpha} (\partial \mathscr{S}/\partial \hat{\Phi}_i^{(\alpha)}) \odot \Lambda_i^{(\alpha)}. \tag{5.3}$$

We note that $\Lambda_i^{(\alpha)}$ is not the same as the time rate of change in the extensive variables in Eq. (5.1). Nevertheless, it may be quite possible to develop a coherent theory of nonlinear irreversible thermodynamics by using the concept of dissipated availability. We remark that we have a formalism of irreversible thermodynamics in the present approach and the present work is an application of the formalism. It appears important to draw another more important distinction between the entropy production as defined by Eq. (1.2) and the dissipated availability. The entropy production (1.2) is the local rate of entropy produced within the system irrespective of its entropy exchange with the surroundings. On the other hand, the availability is associated, as defined originally by Keenan, with the work available to the system in interaction with the surroundings (medium). Of course, it is possible to regard the system and the surroundings as a larger system and try to relate the dissipated availability to the local entropy production, but it appears appropriate to draw a distinction between them, since the availability requires the component parts to be in internal equilibrium.[18] Such a condition is not necessary for the entropy production defined here.

In conclusion, we have proposed a pair of flux evolution equations which account for the current fluctuation phenomenon observed in GaAs in terms of a bifurcation of steady states, as the external field increases in strength. This interpretation offers a new viewpoint to an interesting phenomenon in semiconductors. Through the study presented, we have also shown a piece of evidence for the connection between a nonmonotonic entropy production and instability phenomena in macroscopic systems. This information is, in our opinion, more interesting than the bifurcation mechanism proposed for the experimental data on GaAs, since it enables us to glimpse the potential usefulness of the entropy production formulated in the present series of work on irreversible thermodynamics.

[1] S. Kabashima, H. Yamazaki, and T. Kawakubo, J. Phys. Soc. Jpn. **40**, 921 (1976).
[2] J. B. Gunn, Solid State Commun. **1**, 188 (1963).
[3] P. N. Butcher, Rep. Prog. Phys. **30**, 97 (1963).
[4] M. Shaw, H. Grubin, and P. Solomon, *The Gunn–Hilsum Effect* (Academic, New York, 1979).
[5] S. R. de Groot and P. Mazur, *Nonequilibrium Thermodynamics* (North–Holland, Amsterdam, 1962).
[6] (a) Lord Rayleigh, Proc. Math. Soc. London **4**, 357 (1873); *Theory of Sound* (MacMillan, London, 1877), Vol. 1, p. 78; (b) L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).

[7](a) B. C. Eu, J. Chem. Phys. **73**, 2958 (1980); (b) **74**, 3006 (1981); (c) **74**, 6362 (1981); (d) **74**, 6372 (1981); (e) B. C. Eu and Y. Okamura, *ibid.* **74**, 4663 (1981); (f) B. C. Eu, *ibid.* **76**, 2618 (1982); (g) *ibid.* **79**, 2315 (1983); (h) Phys. Lett. A **96**, 29 (1983).
[8]B. C. Eu, J. Chem. Phys. **75**, 4031 (1981).
[9]B. C. Eu and A. S. Wagh, Phys. Rev. B **27**, 1037 (1983).
[10]These definitions of nonlinear mobilities are in analogy to the linear mobility defined for carriers. See, for example: (a) J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University, London, 1972); or (b) B. R. Nag, *Electron Transport in Compound Semiconductors* (Springer, Heidelberg, 1980).
[11]E. Pytte and H. Thomas, Phys. Rev. **179**, 43 (1968).
[12]E. A. Coddington and N. Levinson, *Theory of Ordinary Differential Equations* (McGraw–Hill, New York, 1955).
[13]T. Kawakubo (private communication). Professor Kawakubo communicated to us that his data on the current–field characteristic (the filled circles in Fig. 4) were the readings on an ammeter which could not follow the fluctuations. Therefore, they should be regarded as averages of fluctuating currents.
[14]D. H. Sattinger, *Topics in Stability and Bifurcation Theory* (Springer, Heidelberg, 1973).
[15]K. Nakamura, J. Phys. Soc. Jpn. **38**, 46 (1975).
[16]J. Keizer, J. Chem. Phys. **74**, 1350 (1981).
[17]For a nonmonotonicity of the entropy production in nonequilibrium states, see also P. H. Richter, P. Rehmus, and J. Ross, Prog. Theor. Phys. **66**, 385 (1981).
[18]J. H. Keenan, *Thermodynamics* (M.I.T., Cambridge, 1966).
[19]P. Salamon and R. S. Berry, Phys. Rev. Lett. **26**, 1127 (1983).