Thermodynamics of Nonlinearity and Noise in Diodes

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The irreversible thermodynamics of a nonlinear diode are discussed by considering a circuit in which a biased diode exchanges noise power with a linear resistor at a different temperature. By applying the Onsager reciprocity relations to the two cross terms involving the rectification of thermal noise, and the generation of current noise by the diode, respectively, an equation is obtained relating the nonlinearity of the diode and a parameter which specifies its current-noise behavior. The implications of this equation are discussed in relation to the existence of a maximum value of the nonlinearity. The analysis predicts that a reverse current will flow through the diode when the resistor is at a lower temperature, and an experiment to confirm this is reported briefly.

I. INTRODUCTION

It has been suspected for many years that there may exist some kind of thermodynamic limit on the degree of nonlinearity which can be realized in a diode, that is, a passive, dissipative, two-terminal circuit element. The suspicion arises from the fact that the rectification process in such diodes usually involves some mechanism in which electrons are sorted (e.g., by a barrier) according to their energy, and that there is a natural energy spread equal to $kT$, which limits the resolution of such a sorting mechanism. It is clear that if such a limit exists, it can apply only near zero-bias voltage, for a “black box” having an arbitrarily large nonlinearity between its two terminals can be synthesized using a circuit involving a diode and an amplifier which derives its power supply from the terminal voltage itself. In this paper we show, not that such a limit exists, but that diodes with large nonlinearities must also develop a great deal of electrical noise, and that this imposes restrictions on the type of rectification mechanism involved. In arriving at this proof, we deduce equations for the transport of heat (as noise power) and electricity in a circuit consisting of a diode connected to a resistor at a different temperature. By applying the Onsager reciprocity relations to these equations, we derive a thermodynamic relationship, which is apparently new and of considerable generality, among the parameters of the diode. One of the equations makes the somewhat surprising prediction that a current should flow spontaneously through the diode in the reverse (high-resistance) direction when the resistor is at a lower temperature than the diode. An experiment to verify this result is reported briefly.

II. THEORY

For the purposes of this paper we consider a diode, as defined above, having bias-dependent differential conductances $g_1(0)$ at dc, and $g_1(f)$ at frequency $f$. The diode will act as a source, at the very least, of thermal noise currents. In addition, the rectification of noise voltages may produce a dc signal if the diode has an asymmetrical nonlinearity. Thus, the diode can be approximated, for small signals, by equivalent circuits of linear conductance $g_1(0)$ and $g_1(f)$, shunted by a dc current generator of value $I'$, and a noise-current generator of spectral density $S'_C(f)$, respectively, as shown in Fig. 1. The currents $I$ and $S'_C(f)$ which actually flow will, of course, depend on the external circuit, as well as on the strengths of the internal generators; in addition, we expect that $I'$ will depend, as a result of rectification effects, on the noise voltage spectral density $S_C(f)$ existing across the diode terminals, and that $S'_C$ will depend on the dc terminal voltage $V$, as a result of shot noise. Carrying out an expansion about $V = S_C = 0$, and neglecting terms of order $V^3, S_C^3, V S_C$, and higher, we write

$$I' = I_0 + \frac{1}{2} \int g_2(f) S_C(f) df$$

$$S'_C(f) = S_0(f) + g_2(f) V.$$  

Here we have defined $\frac{1}{2} g_2(f)$ as the derivative of $I'$ with respect to the mean square noise voltage at frequency $f$, that is, $g_2(f) = \partial I'/\partial [S_C(f) df]$. Similarly, we have put $g_2(f) = S'_C(f)/\partial V$, the derivative of the noise-current source with respect to dc voltage. We note that $g_2$ and $g_2 df$ have the dimensions $(A \cdot V^{-2})$ and $(A^2 \cdot V^{-1})$, respectively, and that $g_2$, which describes the rectification process, is obviously related to the nonlinearity of the diode. We have neglected any reactive component of the diode admittance, as this can always be supposed tuned out by an external susceptance (if necessary nonlinear) of opposite sign. The constant $S_0$ can be identified with the spontaneous Johnson noise of the diode, while $I_0$ represents a spontaneous constant dc whose significance is discussed below. The dc and noise currents which actually flow, when the diode is connected to an external circuit having noise

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2 We thus exclude devices such as electrolytic rectifiers, or thermionic diodes with different anode and cathode temperatures. In such cases, the flow of energy available from, or required by, the mechanism of the device, vitiates the following arguments.
3 The spectral density of a variable is defined as the mean square fluctuation per unit bandwidth.
conduction $G_{f}$, are of course given by

$$I = I' + g_{1}(0) V$$

and

$$S_{1}(f) = \left\{ \frac{G'(f) - g_{2}^{2}(f)}{G(f) + g_{1}(f)} \right\} S'(f) + g_{2}^{2}(f) S_{1}(f).$$

When (1) and (2) are substituted in (3) and (4), it will be seen that the latter contain, in addition to the self-effect terms involving $g_{1}(0)$ and $g_{1}(f)$, cross terms involving $g_{2}(f)$ and $g_{3}(f)$, which result from interaction between the dc and noise signals. We expect that the last two may be connected by some kind of reciprocity relation, and to investigate this we imagine the diode $D$, every part of which is at temperature $T_{D}$, to exchange noise power ($= $ heat) with a linear resistor $R$ at temperature $T_{R}$, through the circuit shown in Fig. 2. The lossless bandpass filter connecting $D$ and $R$ has the following properties:

1. It presents zero impedance to the diode, except over some narrow frequency band from $f$ to $f + 6f$. This ensures that the direct current $I$ does not flow through $R$, and that the dc voltage across the battery (which we suppose to be thermodynamically reversible) is equal to the diode dc voltage $V$. It also ensures that the transmission of noise power between $D$ and $R$ is limited to a range over which the quantities $g_{1}(f)$ and $g_{2}(f)$ may be considered constant.

2. It acts as an impedance transformer, if necessary, so that within the pass band the conductance $G$ presented to the diode terminals is equal to $g_{0}(f)$, the value of $g_{1}(f)$ when $V = 0$, and the circuit is exactly matched for the transmission of noise power between $D$ and $R$ when $V = 0$.

In order to apply irreversible thermodynamics to this circuit, we must calculate the total rate of entropy production $S$. Entropy is produced by the dissipation of the dc power $IV$ in the diode at temperature $T_{D}$, by the generation of the net noise-power flow $W_{n}$ at $T_{R}$, and by its dissipation at $T_{D}$. Hence, we have

$$S = \left( \frac{IV}{T_{D}} \right) - \left( \frac{W_{n}}{T_{R}} \right) + \left( \frac{W_{n}}{T_{D}} \right)$$

$$\approx \left( \frac{1}{T_{D}} \right) \left[ IV + W_{n}(T_{R} - T_{D}) / T_{D} \right].$$

if we assume $T_{R} - T_{D} \ll T_{D}$. Thus, if we choose $I$ and $W_{n}$ to be the thermodynamic "fluxes" in the system, the corresponding "forces" are $V$ and $(T_{R} - T_{D}) / T_{D}$.

Relations between the forces and fluxes can be obtained as follows, in terms of the definitions (1) and (2). By Nyquist's theorem, the power available from $R$, through the filter, is $kT_{D}g_{2}^{2}$, where $k$ is Boltzmann's constant. The quadratic nonlinear term in the diode characteristic, represented by $g_{2}$, does not affect the dissipation of noise power in $D$. This is true because the second harmonic currents, to which it gives rise, cause no second harmonic voltages, in view of the properties of the filter, and because, under the matched conditions which we have assumed, the power transfer is insensitive to the small mismatch resulting from the change in noise conductance of $D$ when a bias is applied. Thus the power delivered to $D$ is also $kT_{D}g_{2}^{2}$. The power available from $D$, when $V = 0$, is similarly equal to $kT_{D}g_{2}^{2}$, despite the nonlinearity. Thus, we find

$$S_{o}(f) = 4kT_{D}g_{2}^{2}f.$$ (6)

In calculating the power available when $V \neq 0$, however, it is necessary to take account of the variation of $g_{1}(f)$ with $V$, because the term $g_{1}V$ is defined in such a way as to take account only of the variation of $S_1$. The power available from $D$ in this case is

$$S_{o}(f) = \frac{1}{2} \left[ \frac{S_{o}(f)}{g_{0}(f)} \right] + V(\partial / \partial V) \left[ \frac{S_{o}(f)}{g_{0}(f)} \right] \partial f$$

$$= kT_{D}g_{2}^{2}f + \left[ \frac{1}{4g_{0}(f)} \right] \left[ g_{0}(f) - 4kg_{2}^{2}f^{2} \right] \partial f \cdot V.$$ (7)

where we have substituted (6) for $S_{o}$, and have written $g_{1}^{2}(f) = \partial g_{1}(f) / \partial V$. This last quantity is related to the nonlinearity of the diode, but is not necessarily equal to $g_{2}(f)$. Equation (7) also gives the noise power delivered to $R$, since the matching is not upset (to first order in $V$) by the change in $g_{1}(f)$. Thus, the net noise-power flow from $R$ to $D$ is

$$W_{n} = kT_{D}g_{2}^{2} \left[ \frac{1}{2} \left( \frac{T_{R} - T_{D}}{T_{D}} \right) \right]$$

$$+ \left[ \frac{1}{4g_{0}(f)} \right] \left[ 4kT_{D}g_{2}^{2}(f) - g_{0}(f) \right] \partial f \cdot V.$$ (8)

When $V = 0$, the quantity $S_{o}(f)$ entering into Eq. (1) is equal to

$$S_{o}(f) = 4kT_{D}g_{2}^{2} \left[ \frac{G(f) + T_{D}g_{2}^{2}(f)}{g_{0}(f) + G(f)} \right],$$

which reduces to $k(T_{D} + T_{D}) / g_{0}(f)$, because of our assumption of exact matching. If in addition $T_{R} - T_{D} = 0$, then we know that $I$ must be zero. If it were not, the fact that the dc conductance of the diode is finite would


permit useful work to be extracted continuously, e.g., by an electric motor; this process is forbidden by the second law of thermodynamics. Consequently, we find that \( I_0 \) in Eq. (1) must have the value \(-\frac{1}{2}g_0(f)S_0\delta f\), or

\[
I_0 = -kT_0\delta g_0(f)/g_0(f).
\]

Thus, the significance of \( I_0 \) becomes clear: it is the constant negative current source which must be supposed to exist so that, in thermal equilibrium, the current caused by the rectification of externally generated noise shall just be balanced, and no net current shall flow. This current has rather implausible properties, as it depends on the joint properties of the diode and the external circuit, and flows in an unexpected sense (the high-resistance direction through the diode). There is no doubt of its physical existence, however, as shown by the experiment described below.

When \( V \) is not zero, \( S_0 \) changes slightly because of the changes in \( g_1(f) \) and \( S_1'(f) \). The new value is

\[
S_0 + 4k[G(f)T_0 + g_0(f)T_0^2]V(\partial \delta V/\partial V)^2[G(f) + G(f)]^{-2}V(\partial \delta V/\partial V)S_1'(f).
\]

Since we have assumed \( G(f) = g_0(f) \), this gives

\[
S_0 = [k(T_0 + T_0^2)]g_0(f)[1 - \frac{1}{2}g_1(f)/g_0(f)]V + \frac{1}{2}g_0(f)/g_0(f)]V.
\]

By virtue of Eqs. (1), (9), and (10), Eq. (3) now reads

\[
I = \{g_0(f) - \frac{1}{2}g_0(f)g_1(f)kT_0\delta f/g_0(f)^2\}
\]

\[+ \frac{1}{2}[g_0(f)g_1(f)\delta f/g_0(f)^2]V
\]

\[+ \frac{1}{2}g_0(f)/g_0(f)kT_0\delta f/[T_0 - T_0^2]/T_0^2
\]

which we retain only first-order terms, and note that the variation of \( g_0(f) \) gives a field of order \( V^2 \). Thus, we have replaced \( g_1(f) \) by \( g_0(f) \), its zero-bias value.

Equations (8) and (11) express the relations between \( W_0 \) and \( I \) (the thermodynamic fluxes) and \( (T_0 - T_0^2)/T_0 \) and \( V \) (the conjugate forces) in a form suitable for the application of the Onsager reciprocity relations. These relations require the equality of the coefficients of cross terms relating forces and fluxes; in the present case, they are the coefficients of \( V \) in (8) and of \( (T_0 - T_0^2)/T_0 \) in (11). Thus, we obtain

\[
g_0(f) = 2kT_0[2g_0'(f) - g_0(f)],
\]

which is the desired thermodynamic relation among the properties of the diode.

We note that, although both \( g_0(f) \) and \( g_0'(f) \) are related to the quadratic nonlinearity, they are not exactly the same quantity. If \( V \) represents the instantaneous value of a signal voltage at frequency \( f \), then \( g_0(f) \) is given by \( \partial g_0(f)/\partial V \), whereas \( g_0'(f) \) is equal to \( \partial g_0(f)/\partial V \), the corresponding derivative with respect to the dc bias \( V \). However, in many cases the two quantities are equal, and when this is so, Eq. (12) can be simplified further. For example, if the frequency is sufficiently low, so that \( i \), the signal current at \( f \), depends on \( v \) in the same way as \( I \) varies with \( V \), then the total current can be expanded, for small voltages, to give

\[
I + i = I_0 + (V + v)(\partial I/\partial V) + \frac{1}{2}(V + v)^2(\partial^2 I/\partial V^2) + \cdots.
\]

In this case we see that the two coefficients are given by

\[
g_0'' = g_0 - \partial^2 I/\partial V^2.
\]

It can also be shown that, if a frequency-dependent voltage attenuation \( A(f) \) is interposed before a diode obeying (13), the quantities measured at the input to the attenuator are given by

\[
g_0'' = g_0 - A^2(f)(\partial^2 I/\partial V^2).
\]

Thus, in either of these practically important cases, Eq. (12) reduces to

\[
g_0'(f) = 2kT_0g_0(f).
\]

The physical content of this equation can be made more explicit if the noise term is defined in relation to \( I \), rather than to \( V \). For this purpose we rewrite Eq. (2) in terms of the spectral density \( 2Iq \) of the shot noise due to a current \( I \), carried by independent electrons of charge \( \pm q \). Thus, we write

\[
S_1'(f) = S_0(f) + 2Iq\theta(f),
\]

so that \( \theta \) is the ratio of the noise actually produced by \( I \) to that which would result from full shot noise. Furthermore, when \( \delta f \) is small, we may write Eq. (11) in the form \( I = g_0(0)V \), to a sufficient degree of approximation, so that Eq. (16) becomes

\[
g_0'(f)/g_0(f) = q\theta(f)/kT_0.
\]

This equation is the central result of the present paper. It relates three quantities \( g_2, g_1, \) and \( \theta \), each of which depends on the detailed structure and mechanism of the diode, in a way which involves only the carrier charge and the diode temperature, and which has, apparently not been suspected previously. Because of the way in which it was derived, it is, of course, completely independent of the mechanism of the diode.

### III. DISCUSSION AND EXPERIMENT

Equation (18) gives at once some information about the maximum degree of nonlinearity, represented by

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7 See Ref. 4, p. 39.

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When \( \delta f \) is not small, \( g_0(0) \), as we have defined it, is no longer quite independent of the rf (= noise frequency) properties of the external circuit. The changes in \( g_0(0) \) result from the fact that the mechanism (see Ref. 6) which gives rise to the small current \( I_0 \), and depends on \( \delta f \), also varies with \( V \). Such subtleties are beyond the scope of this paper.
\( g_0/g_0b \), which can be achieved by a given type of rectification mechanism. For most types of diode, the nonlinearity and noise are generated by electrons traversing some kind of barrier, and the actual current \( I \) can be found as the difference between the currents, \( I_1 \) and \( I_2 \), due to charge carriers crossing the barrier in opposite directions. If the carriers composing each of these currents behave statistically independently, the noise produced is proportional to their sum. Thus, we have

\[
\theta(0) = \frac{\left( \frac{\partial I_1}{\partial V} + \frac{\partial I_2}{\partial V} \right)}{\left( \frac{\partial I_1}{\partial V} - \frac{\partial I_2}{\partial V} \right)}. \tag{19}
\]

Different rectification mechanisms can be considered in the light of this equation.

In the simplest case, such as a Schottky barrier free of image-force and tunneling effects, one of the currents is independent of \( V \), and so \( |\theta(0)| = 1 \); Eq. (18) may be verified by direct calculation in this case. If the barrier height is modulated by image force effects, \( \partial I_1/\partial V \) and \( \partial I_2/\partial V \) will have opposite signs, and so \( |\theta(0)| < 1 \). For an ideal \( p-n \) junction, the situation is slightly complicated by the possibility that both hole and electron currents contribute to \( I \). For each carrier alone, however, the current may be split into a voltage-dependent part due to carriers diffusing up the potential gradient, and a constant part due to minority carriers diffusing to the junction. Thus, \( \theta = 1 \) for each carrier taken alone, and so also for the total current. In tunnel diodes, however, the situation may be different, because the application of a bias voltage has two distinct effects:

(1) It changes the number of electrons which are able to tunnel, increasing the number available for \( I_1 \), say, and reducing that for \( I_2 \).

(2) It changes the barrier, so altering the probability of an electron tunneling (in either direction) through it. This latter effect affects \( I_1 \) and \( I_2 \) in the same sense, and tends to reduce the value of \( (\partial I_1/\partial V - \partial I_2/\partial V) \). Indeed, if it were the only effect, this quantity would be zero. Thus, the modulation of the tunneling probability can allow \( \theta > 1 \); hence, \( g_0/g_0b \) may exceed \( g/kT_B \) for a tunnel diode.

If the motions of the charge carriers are not independent, the resulting correlation produces additional effects. Usually this correlation is negative; the crossing of the barrier by an electron reduces the probability that other electrons will do so, and \( \theta \) is reduced. This effect can be produced by a positive series impedance, for example. Alternatively, there may be an Ohmic shunt path, through which a highly correlated part of the current is carried without shot noise; the value of \( \theta \) is again reduced. On the other hand, \( \theta \) can exceed unity, if there is a positive correlation among the motions of the electrons so that they tend to move in groups, of average charge \( q\theta \). It is very difficult to see how such a tendency could arise, except in the tunneling of superconducting electron pairs. A negative series resistance could have this effect, but would violate our assumption that the diode is passive, and that \( V \) is small. Thus, the condition \( g_0/g_0b \leq g/kT_B \) can be violated only under well-defined conditions.

The fact that (12) is an equation, rather than an inequality, allows a further conclusion to be drawn: There can be no shot noise, near zero bias, without a corresponding nonlinearity. The converse, although not necessarily true in all cases, does hold unless \( 2g_0 = g_3 \). In particular, it is true that any nonlinearity, for which Eq. (14) or (15) is true, must be accompanied by shot noise. It should be noted, in this connection, that the so-called ‘‘1/f’’ noise, or any other type of noise due to conductivity modulation, is irrelevant to the argument, since such sources of noise always vary as a power of the current which is higher than the first, and consequently became negligible compared with the shot and Johnson noise as the current is reduced. Also excluded from consideration are all devices, such as bolometers or self-heated thermocouples, where the nonlinear effects have a thermal origin; Eq. (5) is not satisfied in such cases.

Although we have considered, up to this point, only two-terminal nonlinear circuit elements, there is nothing in Eqs. (1)–(5), or in the subsequent argument, to exclude four-terminal transducers, in which a two-terminal nonlinearity cannot be identified for analysis. An example of such a transducer would be a motor-generator set, in which a series-field motor, free of Coulomb friction, drives a similarly idealized dc generator having a permanent magnet field. Since the torque of the motor depends on the square of the current, a dc output can be derived from a noise input. For this system, however, it can be shown that \( 2g_3 - g_3 = 0 \), so that \( g_3 = 0 \). Since this is true even though both machines have some electrical losses, it follows that the rotation of the series machine does not affect its noise.

It will be noted that the circuit of Fig. 1 has properties which are formally identical to a conventional thermocouple circuit, although the mechanism is quite different and the effects will generally be much smaller. In each circuit, a temperature difference and an applied voltage each give rise to a current both of electricity and of heat. The analysis which we have given is closely analogous to the usual derivation of Thomson’s second relation between the Seebeck and Peltier coefficients. Each circuit, though not reversible in the thermodynamic sense, can drive heat or charge in either direction. In the case of the diode, this is somewhat surprising, as it means that, when the load \( R \) is colder than the diode \( D \), current flows as a consequence through \( D \) in the high-resistance direction, because the rectified noise is not enough to compensate the spontaneous current \( i_0 \).

Despite its implausibility, we have been able to

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The Diffusion and Solubility of Phosphorus in CdTe and CdSe

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Measurements of the solubility and diffusion of P in CdSe from 800°–1000°C and in CdTe at 900° and 950°C as a function of cadmium partial pressure were made using radiotracer techniques. In addition, electrical measurements were made on some P-doped samples of both systems. The phosphorus solubility is highest at a given temperature under maximum cadmium pressure. It is suggested that under these conditions the phosphorus is a substitutional acceptor atom on a chalcogen site that is highly compensated by a donor defect with interstitial Cd donors a likely possibility. The diffusion results are similar to that observed for the chalcogen self-diffusion and are not inconsistent with an interstitial mechanism.

I. INTRODUCTION

Electrically, phosphorus and the other column V elements, As and Sb, play a unique role in the Cd chalcogenides. Whereas the other common acceptor impurities, such as the column I elements, Li, Na, Cu, Ag, etc., appear to be electrically inactive following a firing of the compound under Cd pressure, the column V impurities retain their acceptor action. In particular, recent studies have shown that P in the CdTe2 and ZnTe vibrations creates a shallow acceptor level, and in CdTe incorporation of phosphorus can render the system strongly p-type when fired under saturated cadmium pressure. In CdS and CdSe, incorporation of these impurities results in high-resistivity material, even when fired in Cd. Since

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these impurities appear to be heavily compensated under these conditions, further studies into the diffusion and incorporation mechanisms of these atoms as a function of pressure and temperature are warranted.

In this paper some experiments on the solubility and diffusion of P in CdSe and CdTe are reported. Although more work will be needed in order to establish definitive physical models, the data presented will be of value to those interested in controlling the electrical characteristics of the II–VI compounds.

II. EXPERIMENTAL DETAILS

The general procedure used in obtaining the diffusion profiles has been reported elsewhere. The radioactive1 P was obtained in an HCl solution which was diluted with triple distilled H2O to 1/100 of the original strength. The desired amount (usually about 0.02 ml) of the radioactive solution was pipetted into a quartz tube (4 mm i.d.) followed by 0.1 ml of HNO3.