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NON-LINEAR THERMAL FLUCTUATIONS IN A DIODE

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Synopsis

As an example of non-linear noise the fluctuations in a circuit consisting of a diode and a condenser C are studied. From the master equation for this system the following results are derived.

(i) The equilibrium distribution of the voltage is rigorously Gaussian, the average voltage being equal to the contact potential of the two electrodes.

(ii) The ordinary I–V characteristic of the diode is found in the limit $C \to \infty$.

(iii) An expansion in e^2/kTC is used to find the spectral density of the fluctuations to first order. It is shown that to this order the Fokker-Planck equation gives the same result.

(iv) Another approximation method leads to an expansion of the fluctuation spectrum in inverse powers of the frequency. It is rigorously shown that the first term in this expansion is not affected by the presence of the non-linearity.

(v) The so-called fluctuation-dissipation theorem is not valid beyond the linear approximation.

(vi) The expansion of the fluctuation spectrum in e^2/kTC can be calculated to all orders. However, the complete spectrum contains additional terms, which do not show up in this expansion, as they are of infinite order in e^2/kTC.

1. *Introduction.* The problem of noise in non-linear dissipative systems has recently been studied by several authors, but so far no unique result has emerged. Since MacDonald's first paper[1]) one usually studies a simple electric circuit consisting of a non-linear element and a condenser; the problem is to find the power spectrum of the current fluctuations in the circuit. There is no agreement either on the physical principles from which to start out, nor on the approximations to be used in the calculation. For this reason Alkemade [4]) gave an explicit calculation for a specific example, namely the case that the non-linear element is a vacuum diode. However, he only calculated the high-frequency limit, which unfortunately turns out to be insensitive to the presence of the non-linearity. This permitted only a very incomplete check on the existing theories. To make a more detailed check possible we here present a calculation of the entire fluctuation spectrum of the vacuum diode.

Outline of the calculation. In section 2 the basic master equation is established, which governs the behaviour in time of the probability

distribution of the charge on the condenser. The remaining work consists in solving this equation and is therefore mathematics. In particular, the equilibrium distribution is found in section 3, and turns out to be rigorously Gaussian.

Although it does not seem impossible to solve the master equation rigorously, we are mainly interested in an approximate treatment, because it is more instructive. We only use systematic approximations, i.e., expansions in terms of a well-defined parameter. Three different expansions are used according to what one is interested in. The first one is an expansion in powers of e^2/kTC (C is the capacity of the condenser and e the absolute value of the electron charge), the voltage V being kept constant. The leading term in this expansion corresponds to the case of negligible fluctuations and will therefore enable us to find the phenomenological I–V characteristic of the non-linear element.

A second expansion is used for studying the fluctuations in equilibrium. This is again an expansion in e^2/kTC, but the voltages occurring in these fluctuations are themselves of order $(e^2/kTC)^{\frac{1}{2}}$. The leading term now amounts to the linear approximation, while the higher terms describe the influence of the non-linearity on the fluctuations. In this way we find in section 6 the power spectrum of the fluctuations to the first order in e^2/kTC.

The high frequency limit of the fluctuation spectrum can be found by a much simpler method. Accordingly, we use a third expansion in section 7, namely in powers of the reciprocal frequency rather than in e^2/kTC. In this way Alkemade's result is rederived and the higher terms can also be found.

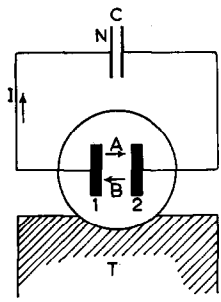
In section 8 the Fokker-Planck equation for the present problem is formed, and is shown to lead to the correct results, provided one does not go beyond the first power of e^2/kTC.

In section 9 we study the fluctuations that occur while the system is in the process of approaching equilibrium. It appears that they depend on their initial values, so that no general rule can be given for them. In particular, it is shown that the fluctuation-dissipation theorem does not apply to the non-linear case.

Finally, in section 10 a more powerful method for solving the master equation is employed to find the fluctuation spectrum to all orders of e^2/kTC. Yet, even this complete series expansion does not constitute a rigorous solution. The reason is that the rigorous expression for the fluctuation spectrum contains a part that is not analytic in e^2/kTC; it can be shown however, that this part is extremely small in any realistic case.

Note. A preliminary draft of this paper has been circulated in mimeographed form. The present version differs considerably from it; moreover the detailed discussion of earlier literature has been omitted.

2. *The master equation.* Following MacDonald [1]) we consider a circuit consisting of a condenser C and a non-linear dissipative element, in contact with a heat bath with temperature T. Following Alkemade [4]) we take for the non-linear element a vacuum diode consisting of two plane parallel electrodes, 1 and 2, at a short distance from each other *). The two electrodes (and the two halves of the circuit connected with them) are supposed to consist of two different metals with different work functions W_1 and W_2.



More specifically we suppose that electrode 1 operates under saturation conditions; that is, it emits electrodes at a constant rate independent of the potential difference. The number of electrons jumping per unit time from 1 to 2 is according to Richardson's formula

$$A = \frac{4\pi m}{h^3}(kT)^2 \, \mathrm{e}^{-\frac{W_1}{kT}} \cdot O, \tag{1}$$

where O is the area of the electrodes.

The electrons emitted by electrode 2 can only reach 1 when they have a sufficient kinetic energy to overcome the potential difference. Let N be the number of excess electrons in that part of the circuit that is connected with electrode 1; then the voltage is $-eN/C$. The electrostatic energy of the system is $e^2N^2/2C$, so that an electron can only jump from 2 to 1 when its kinetic energy after leaving electrode 2 is at least **).

$$\frac{e^2}{2C}(N+1)^2 - \frac{e^2}{2C}N^2 = \frac{e^2}{C}(N+\tfrac{1}{2}).$$

The probability that such an electron leaves 2 during $\mathrm{d}t$ is

$$B \, \mathrm{e}^{-\frac{e^2}{kTC}(N+\frac{1}{2})} \, \mathrm{d}t, \tag{2}$$

where

$$B = \frac{4\pi m}{h^3}(kT)^2 \, \mathrm{e}^{-\frac{W_2}{kT}} O = A \, \mathrm{e}^{-\frac{W_1 - W_2}{kT}}.$$

*) MacDonald [2]) mentioned the metal-oxide rectifier as an example of a non-linear element. This is mathematically equivalent to Alkemade's diode but less easy to visualize.

**) This argument has been communicated to me by Alkemade.

Let $P(N)$ be the probability that at time t there are N excess electrons on 1. The rate of change of $P(N)$ is determined by the transition probabilities (1) and (2); which leads to the *master equation*

$$\frac{\partial P(N)}{\partial t} = AP(N+1) - AP(N) + \\ + B\,e^{-\frac{e^2}{kTC}(N-\frac{1}{2})}\,P(N-1) - B\,e^{-\frac{e^2}{kTC}(N-\frac{1}{2})}\,P(N).$$

We shall use the abreviations

$$\frac{e^2}{kTC} = \varepsilon, \qquad \frac{B}{A}\,e^{-\frac{e^2}{2kTC}} = \zeta = e^{\eta-\frac{1}{2}\varepsilon},$$

so that

$$\eta = \frac{W_1 - W_2}{kT}.$$

(ε is the ratio of $e^2/2C$ – the electrostatic energy of the condenser if charged with one electron – and $\frac{1}{2}kT$; clearly ε must be very small if any fluctuations are to occur.) With these abbreviations the master equation becomes

$$\frac{1}{A}\frac{\partial P(N)}{\partial t} = P(N+1) - P(N) + \zeta\{e^{-\varepsilon(N-1)}\,P(N-1) - e^{-\varepsilon N}\,P(N)\}.$$

The calculation will be greatly simplified by the use of an operator E defined by

$$\mathsf{E}f(N) = f(N+1), \quad \mathsf{E}^{-1}f(N) = f(N-1).$$

With its aid the master equation may be written

$$\frac{1}{A}\frac{\partial P}{\partial t} = \{\mathsf{E} - 1 + \zeta(\mathsf{E}^{-1} - 1)\,e^{-\varepsilon N}\}P = \mathsf{F}P, \tag{3}$$

where F denotes the operator $\{\ \}$.

This equation will be solved mathematically. From a physical point of view, of course, (3) is not quite exact in several respects. *Firstly*, it neglects the time of flight of the electrons between both electrodes. *Secondly*, N is allowed to take all integral values from $-\infty$ to $+\infty$, although the number of electrons is finite; moreover, the assumption of saturation breaks down for very large negative N. *Thirdly*, no correlation between the individual jumps of the electrons is taken into account; in particular, the temperature is supposed to be kept rigorously constant by the heat bath, independent of the number of bombarding or emitted electrons. However, it seems likely that all these effects can be made arbitrarily small by a suitable choice of diode, and that no essential features are lacking in our statistical problem.

3. *The equilibrium state.* The equilibrium distribution is found from

$$\{\mathsf{E} - 1 + \zeta(\mathsf{E}^{-1} - 1)\, \mathrm{e}^{-\varepsilon N}\}\, P^{\mathrm{eq}} = 0.$$

This equation can be factorized,

$$(\mathsf{E} - 1)\,\{1 - \zeta\mathsf{E}^{-1}\, \mathrm{e}^{-\varepsilon N}\}\, P^{\mathrm{eq}} = 0,$$

which shows that

$$\{1 - \zeta\mathsf{E}^{-1}\, \mathrm{e}^{-\varepsilon N}\}\, P^{\mathrm{eq}}$$

must be a constant independent of N. Moreover, as P^{eq} vanishes for $N \to \infty$, the constant must be zero. Hence

$$P^{\mathrm{eq}}(N) = \zeta\, \mathrm{e}^{-\varepsilon(N-1)}\, P^{\mathrm{eq}}(N - 1).$$

From this one easily finds, for both positive and negative N,

$$\begin{aligned} P^{\mathrm{eq}}(N) &= \zeta^N\, \mathrm{e}^{-\frac{1}{2}\varepsilon N(N-1)}\, P^{\mathrm{eq}}(0) \\ &= \mathrm{e}^{-\frac{1}{2}\varepsilon N^2 + \eta N}\, P^{\mathrm{eq}}(0). \end{aligned} \tag{4}$$

We shall define

$$Z = \mathsf{S}\, \mathrm{e}^{-\frac{1}{2}\varepsilon N^2 + \eta N}, \tag{5}$$

where S denotes a summation over N from $-\infty$ to $+\infty$. Clearly Z has the form of a grand canonical partition function, and

$$P^{\mathrm{eq}}(0) = 1/Z.$$

It is possible to give a rigorous expression for Z in terms of theta-functions *)

$$Z = \vartheta_3\left(-\tfrac{1}{2}i\eta \,\middle|\, \frac{i\varepsilon}{2\pi}\right). \tag{6}$$

It is often more convenient, however, to use an approximation for $\varepsilon \ll 1$, which consists in replacing the summation in (5) with an integration,

$$Z \simeq \int_{-\infty}^{+\infty} \mathrm{e}^{-\frac{1}{2}\varepsilon N^2 + \eta N}\, \mathrm{d}N = \sqrt{\frac{2\pi}{\varepsilon}}\, \mathrm{e}^{\eta^2/2\varepsilon}. \tag{7}$$

This we shall call 'the approximation of continuous N'. How good it is can be seen by comparing it with the exact expression

$$Z = \sqrt{\frac{2\pi}{\varepsilon}}\, \mathrm{e}^{\eta^2/2\varepsilon}\vartheta_3\left(-\frac{\pi\eta}{\varepsilon} \,\middle|\, \frac{2\pi i}{\varepsilon}\right),$$

which is obtained from (6) by applying the functional relation of the theta-functions. The approximation consists in replacing ϑ_3 with 1, thus omitting

*) We use the notation of E. T. Whittaker and G. N. Watson, *A course of modern analysis*, chapter 21.

terms of relative order $e^{-2\pi^2/\varepsilon}$. Such terms vanish for small ε faster than any power of ε.

Clearly (4) is a Gaussian distribution, but for the fact that the variable N is discrete. In the approximation of continuous N the maximum lies at

$$\langle N\rangle^{\mathrm{eq}} = \frac{\eta}{\varepsilon} = \frac{W_1 - W_2}{e^2/C}, \tag{8}$$

and the mean square fluctuation is

$$\langle (N - \langle N\rangle^{\mathrm{eq}})^2\rangle^{\mathrm{eq}} = 1/\varepsilon.$$

The average voltage corresponding to (8) is

$$-\frac{e}{C}\langle N\rangle^{\mathrm{eq}} = \frac{W_1 - W_2}{-e}, \tag{9}$$

which is the contact potential caused by the difference of the work functions. The mean square fluctuation of the voltage is kT/C, as it should.

It can again be checked that the errors in these results due to the approximation of continuous N are small of infinite order of ε. Nevertheless we shall from now on treat N as discrete; the approximation has been used here merely to show that the distribution (4) is in agreement with the usual results.

The master equation (3) is clearly invariant for the substitution

$$N = N_0 + N', \quad \zeta = \zeta' e^{\varepsilon N_0}, \quad P(N) = P'(N'),$$

where N_0 is an arbitrary number. Thus *a shift of the zero point on the N-scale amounts to altering the value of* ζ. We shall employ this invariance by choosing $N_0 = \eta/\varepsilon$, so that $\zeta' = e^{-\frac{1}{2}\varepsilon}$. Then, dropping the primes, one has

$$\frac{1}{A}\frac{\partial P}{\partial t} = \{\mathsf{E} - 1 + (\mathsf{E}^{-1} - 1)\, e^{-\varepsilon(N+\frac{1}{2})}\}\, P = \mathsf{F}P, \tag{10}$$

$$P^{\mathrm{eq}}(N) = \frac{1}{Z} e^{-\frac{1}{2}\varepsilon N^2}, \tag{11}$$

$$Z = \mathsf{S}\, e^{-\frac{1}{2}\varepsilon N^2}. \tag{12}$$

Of course, N now assumes no longer integral values, but rather runs over the set of all integers shifted by a certain fixed amount.

An alternative choice is $N_0 = \eta/\varepsilon - \frac{1}{2}$. Then $\zeta' = 1$, so that (10) takes a simpler form; but in return (11) is less simple and, in particular, one now has $\langle N\rangle^{\mathrm{eq}} = \frac{1}{2}$. This choice was tacitly made by those authors who find for the average charge in equilibrium $-\frac{1}{2}e$. *)

*) Recently A. Marek [7]) has pointed out that an average charge different from zero is at variance with the second law of thermodynamics. Yet his proof does not apply to our present case, because we assumed the two halves of the circuit to consist of different metals. Although this assumption is somewhat unrealistic, it is not inconsistent with the laws of physics, and may therefore be used for a model. Moreover, if the wires and the condenser plates are permitted to be made of different metals, the treatment would be somewhat more complicated but not essentially different.

4. *The macroscopic equation.* In a non-equilibrium state one finds from (10)

$$\frac{\mathrm{d}}{A\,\mathrm{d}t}\langle N\rangle = \mathsf{S}N\frac{1}{A}\frac{\partial P(N)}{\partial t} = \mathsf{S}N\mathsf{F}P = \mathsf{S}P\tilde{\mathsf{F}}N = \langle\tilde{\mathsf{F}}N\rangle,$$

where $\tilde{\mathsf{F}}$ is the adjoint of F:

$$\tilde{\mathsf{F}} = \mathsf{E}^{-1} - 1 + \mathrm{e}^{-\varepsilon(N+\frac{1}{2})}(\mathsf{E} - 1). \tag{13}$$

Thus one gets rigorously

$$\frac{\mathrm{d}}{A\,\mathrm{d}t}\langle N\rangle = -1 + \mathrm{e}^{-\frac{1}{2}\varepsilon}\langle\mathrm{e}^{-\varepsilon N}\rangle. \tag{14}$$

Now the term $\langle\mathrm{e}^{-\varepsilon N}\rangle$ on the right does not depend on the voltage alone, but on the entire shape of the distribution $P(N)$, and moreover on C. That means that the average current through the diode depends on the fluctuations, and on the size of the condenser. Hence (14) cannot be identified with the macroscopic phenomenological current-voltage characteristic of the diode. *The proper way of relating* (14) *with macroscopic features of the diode is by studying the limit of infinite* C, *keeping the voltage* $-eN/C$ *fixed.* Then the fluctuations in the voltage will tend to zero so that (14) becomes

$$\frac{\mathrm{d}}{A\,\mathrm{d}t}\langle N\rangle = -1 + \mathrm{e}^{eV/kT}.$$

Here $V = -eN/C$ is the actual potential difference minus the contact potential. This equation is identical with the familiar form of the I–V characteristic of the diode,

$$I = eA(\mathrm{e}^{eV/kT} - 1). \tag{15}$$

On expanding the exponential,

$$I = \frac{e^2A}{kT}V + \frac{e^3A}{2(kT)^2}V^2 + \ldots,$$

one finds the connection of A with the phenomenological resistance in the linear region,

$$\frac{e^2A}{kT} = \frac{1}{R_0}.$$

5. *Equations for the moments.* From the master equation one finds for the successive moments of N

$$\frac{\mathrm{d}}{A\,\mathrm{d}t}\langle N^p\rangle = \mathsf{S}N^p\mathsf{F}P = \langle\tilde{\mathsf{F}}N^p\rangle.$$

For the present calculations we shall only need the first three moments,

$$\frac{\mathrm{d}}{A\,\mathrm{d}t}\langle N\rangle = -1 + \mathrm{e}^{-\frac{1}{2}\varepsilon}\langle \mathrm{e}^{-\varepsilon N}\rangle, \tag{16a}$$

$$\frac{\mathrm{d}}{A\,\mathrm{d}t}\langle N^2\rangle = 1 + \mathrm{e}^{-\frac{1}{2}\varepsilon}\langle \mathrm{e}^{-\varepsilon N}\rangle - 2\langle N\rangle + 2\mathrm{e}^{-\frac{1}{2}\varepsilon}\langle N\,\mathrm{e}^{-\varepsilon N}\rangle, \tag{16b}$$

$$\frac{\mathrm{d}}{A\,\mathrm{d}t}\langle N^3\rangle = -1 + \mathrm{e}^{-\frac{1}{2}\varepsilon}\langle \mathrm{e}^{-\varepsilon N}\rangle + 3\langle N\rangle + 3\mathrm{e}^{-\frac{1}{2}\varepsilon}\langle N\,\mathrm{e}^{-\varepsilon N}\rangle - 3\langle N^2\rangle + 3\mathrm{e}^{-\frac{1}{2}\varepsilon}\langle N^2\,\mathrm{e}^{-\varepsilon N}\rangle. \tag{16c}$$

Of course, this does not constitute a closed set of equations, since $\langle \mathrm{e}^{-\varepsilon N}\rangle$ involves all higher moments. However, the terms containing these higher moments may be expected to decrease in magnitude, so that it is possible to obtain a closed set by neglecting small terms. In order to do this in a systematic way, we shall use ε as expansion parameter, and anticipate

$$\langle N^p\rangle = O(\varepsilon^{-\frac{1}{2}p}). \qquad (p = 1,2,\ldots) \tag{17}$$

This is suggested by the equilibrium distribution (11), and may therefore be expected to be correct for computing the fluctuation spectrum in equilibrium. It will not apply to non-equilibrium states; that is the reason why a different expansion is used in sections 4 and 9.

In order to make the various powers of ε explicit, we put

$$\langle N^p\rangle = \varepsilon^{-\frac{1}{2}p}\, m_p.$$

Moreover, it will be useful to put $A\varepsilon t = \tau$, so that out time scale increases proportionally to C, in agrement with the increase of the RC-time of the circuit. Using these notations one finds

$$\frac{\mathrm{d}m_1}{\mathrm{d}\tau} = -m_1 + \varepsilon^{\frac{1}{2}}\left[-\tfrac{1}{2} + \tfrac{1}{2}m_2\right] + \varepsilon\left[\tfrac{1}{2}m_1 - \tfrac{1}{6}m_3\right] + O(\varepsilon^{\frac{3}{2}}), \tag{18a}$$

$$\frac{\mathrm{d}m_2}{\mathrm{d}\tau} = 2 - 2m_2 + \varepsilon^{\frac{1}{2}}\left[-2m_1 + m_3\right] + O(\varepsilon), \tag{18b}$$

$$\frac{\mathrm{d}m_3}{\mathrm{d}\tau} = -3m_3 + 6m_1 + O(\varepsilon^{\frac{1}{2}}). \tag{18c}$$

This constitutes a closed set of three equations for the three unknown functions $m_1(\tau)$, $m_2(\tau)$, $m_3(\tau)$. They permit to find $m_1(\tau)$ up to and including terms of order $\varepsilon^{\frac{3}{2}}$, when the initial values $m_1(0)$, $m_2(0)$, $m_3(0)$ are known. Incidentally, the fact that no negative powers of ε appear on the right justifies our assumption (17). It can be shown that the equations for the higher moments are also consistent with (17).

6. *The fluctuation spectrum.* In order to find the fluctuation spectrum one has to compute the auto-correlation function

$$\langle N(0)\, N(t)\rangle^{\mathrm{eq}}.$$

This notation is meant to indicate the following. Let $P(N_0 \mid N, t)$ denote that solution of the master equation that satisfies the initial condition

$$P(N_0 \mid N, 0) = \delta_{N,N_0}.$$

Then the average N at time t, conditional on the initial value N_0, is

$$\langle N(t)\rangle_{N_0} = \mathsf{S} N P(N_0 \mid N, t). \tag{19}$$

The auto-correlation function is obtained by multiplying this with N_0 and averaging over the equilibrium distribution for N_0,

$$\langle N(0)\, N(t)\rangle^{\mathrm{eq}} = \langle N_0 \langle N(t)\rangle_{N_0}\rangle^{\mathrm{eq}} = \mathsf{S}_0 N_0 P^{\mathrm{eq}}(N_0)\ \mathsf{S} N P(N_0 \mid N, t),$$

where S_0 indicates summation over N_0. Thus our main task will be to determine (19), that is, to solve the equations (18) with the initial conditions

$$m_1(0) = \varepsilon^{\frac{1}{2}} N_0, \quad m_2(0) = \varepsilon N_0^2, \quad m_3(0) = \varepsilon^{3/2} N_0^3. \tag{20}$$

First one finds to zeroth order in ε

$$\begin{aligned} m_1(\tau) &= m_1(0)\, \mathrm{e}^{-\tau} \\ m_3(\tau) &= m_3(0)\, \mathrm{e}^{-3\tau} + 3m_1(0)(\mathrm{e}^{-\tau} - \mathrm{e}^{-3\tau}). \end{aligned}$$

Substituting this in (18*b*) one finds to order $\varepsilon^{\frac{1}{2}}$

$$\begin{aligned} m_2(\tau) = m_2(0)\, \mathrm{e}^{-2\tau} &+ 1 - \mathrm{e}^{-2\tau} \\ &+ \varepsilon^{\frac{1}{2}}\{m_3(0) - 3m_1(0)\}\, (\mathrm{e}^{-2\tau} - \mathrm{e}^{-3\tau}) \\ &+ \varepsilon^{\frac{1}{2}} m_1(0)\, (e^{-\tau} - \mathrm{e}^{-2\tau}). \end{aligned}$$

Substituting now in (18*a*) one finds to order ε

$$\begin{aligned} m_1(\tau) = m_1(0)\, \mathrm{e}^{-\tau} &+ \tfrac{1}{2}\varepsilon^{\frac{1}{2}}\, \{m_2(0) - 1\}\, (\mathrm{e}^{-\tau} - \mathrm{e}^{-2\tau}) + \\ &+ \varepsilon m_1(0)\, (\tfrac{1}{2}\tau\, \mathrm{e}^{-\tau} - \mathrm{e}^{-\tau} + 2\mathrm{e}^{-2\tau} - \mathrm{e}^{-3\tau}) \\ &+ \varepsilon m_3(0)\, (\tfrac{1}{6}\mathrm{e}^{-\tau} - \tfrac{1}{2}\mathrm{e}^{-2\tau} + \tfrac{1}{3}\mathrm{e}^{-3\tau}). \end{aligned} \tag{21}$$

One now has to insert the initial data (20), multiply throughout with N_0 and average over the equilibrium distribution. Using the approximation of continuous N one has

$$\langle N_0^2\rangle^{\mathrm{eq}} = \varepsilon^{-1}, \quad \langle N_0^4\rangle^{\mathrm{eq}} = 3\varepsilon^{-2}. \tag{22}$$

The final result is

$$\varepsilon\langle N(0) N(\tau)\rangle^{\mathrm{eq}} = (1 - \tfrac{1}{2}\varepsilon)\, \mathrm{e}^{-\tau} + \tfrac{1}{2}\varepsilon\, \mathrm{e}^{-2\tau} + \tfrac{1}{2}\varepsilon\tau\, \mathrm{e}^{-\tau}. \tag{23}$$

The Wiener-Khintchine theorem now leads to the spectral density of the fluctuations,

$$S_N(\omega) = \frac{2}{\pi}\int_0^\infty \langle N(0)\, N(\tau)\rangle^{\mathrm{eq}} \cos \omega\tau \, \mathrm{d}\tau \tag{24}$$

$$= \frac{2}{\pi\varepsilon}\left[\frac{1-\varepsilon}{1+\omega^2} + \frac{\varepsilon}{4+\omega^2} + \frac{\varepsilon}{(1+\omega^2)^2}\right]. \tag{25}$$

We translate this result to the usual quantities, viz., the frequency $f = \omega/2\pi R_0 C$ and the current $I = e\dot{N}$.

$$S_I(f) =$$

$$= \frac{4kT}{R_0}(2\pi R_0 C f)^2\left[\frac{1-e^2/kTC}{1+(2\pi R_0 C f)^2} + \frac{e^2/kTC}{4+(2\pi R_0 C f)^2} + \frac{e^2/kTC}{\{1+(2\pi R_0 C f)^2\}^2}\right].$$

First remark. In the derivation terms of order $\varepsilon^{\frac{3}{2}}$ and higher have been discarded, Nevertheless (25) is correct up to order ε^2, because no half-integer powers of ε can occur. This is a consequence of the following invariance property. If one changes simultaneously the signs of $\varepsilon^{\frac{1}{2}}$ and of m_1 and m_3 (without changing the sign of N_0), then the equations (18) and also the initial conditions (20) remain the same. Hence the auto-correlation function (23) must remain the same, which means that it cannot contain odd powers of $\varepsilon^{\frac{1}{2}}$.

Second remark. (25) differs from earlier results in that it has a denominator $(1+\omega^2)^2$. This is not a material difference, however, because (25) may also be written as

$$S_N(\omega) = \frac{2}{\pi\varepsilon}\left[\frac{1-\varepsilon}{(1-\frac{1}{2}\varepsilon)^2+\omega^2} + \frac{\varepsilon}{4+\omega^2}\right]. \tag{26}$$

In fact, it will be shown in section 10 that the correct expression for the fluctuation spectrum is indeed of the type

$$S_N(\omega) = \frac{2}{\pi\varepsilon}\left[\frac{c_1}{a_1{}^2+\omega^2} + \frac{c_2}{a_2{}^2+\omega^2} + \ldots\right]. \tag{27}$$

It may also be noted that one actually arrives at (26) rather than (25), if one solves (18) by means of the standard method for linear differential equations *), instead of by successive orders in ε. However, this would be somewhat misleading, because (26) contains some of the higher order terms, but not all.

7. *The high frequency limit.* For high frequencies

$$S_N(\omega) = \frac{2}{\pi\varepsilon}\left[\frac{1}{\omega^2} - \frac{1+2\varepsilon}{\omega^4} + \ldots\right], \tag{28}$$

*) This method was used by M. Lax [5].

or

$$S_I(f) = \frac{4kT}{R_0}\left[1 - \left(1 + \frac{2e^2}{kTC}\right)(2\pi R_0 C f)^{-2} + \ldots\right].$$

The first term constitutes the result of Alkemade [4]). It shows that *the high frequency limit of the current fluctuations is not affected by the presence of the non-linearity*. In this section we shall demonstrate how this result can be found directly, without using an expansion in ε. *)

From the rigorous Wiener-Khintchine formula (24) an asymptotic expansion for large ω may be derived. The appropriate method is the method of stationary phase; it provides the following recipe for obtaining the asymptotic expansion. First expand $\langle N(0)\, N(\tau)\rangle^{\mathrm{eq}}$ formally in powers of τ,

$$\langle N(0)\, N(\tau)\rangle^{\mathrm{eq}} = \langle N(0)^2\rangle^{\mathrm{eq}} + \tau\langle N(0)\, N'(0)\rangle^{\mathrm{eq}} + \ldots.$$

Next, substitute this in (24) and interchange summation and integration,

$$S_N(\omega) = \frac{2}{\pi}\left[\langle N^2\rangle^{\mathrm{eq}}\int_0^\infty \cos\omega\tau\, \mathrm{d}\tau + \langle NN'\rangle^{\mathrm{eq}}\int_0^\infty \tau\cos\omega\tau\, \mathrm{d}\tau + \ldots\right].$$

Finally evaluate the divergent integrals by temporarily inserting a convergence factor $e^{-\sigma\tau}$. This causes the first integral to vanish, while the second integral is equal to $-\omega^{-2}$,

$$S_N(\omega) \simeq -\frac{2}{\pi\omega^2}\langle NN'\rangle^{\mathrm{eq}}.$$

In order to find

$$\langle NN'\rangle^{\mathrm{eq}} = \mathsf{S}_0 N_0 P^{\mathrm{eq}}(N_0)\left\langle\left\{\frac{\mathrm{d}}{A\varepsilon\,\mathrm{d}t}N(t)\right\}_{t=0}\right\rangle_{N_0}$$

we note from (16*a*)

$$\left\langle\left\{\frac{\mathrm{d}}{A\,\mathrm{d}t}N(t)\right\}_{t=0}\right\rangle_{N_0} = -1 + \mathrm{e}^{-\frac{1}{2}\varepsilon - \varepsilon N_0}.$$

Hence

$$\langle NN'\rangle^{\mathrm{eq}} = \frac{1}{\varepsilon Z}\mathsf{S}_0 N_0^{-\frac{1}{2}\varepsilon N_0^2}\left(-1 + \mathrm{e}^{-\frac{1}{2}\varepsilon - \varepsilon N_0}\right) = -\frac{1}{\varepsilon},$$

which gives the first term of (28).

For the total asymptotic expansion of $S_N(\omega)$ one finds in the same way

$$S_N(\omega) \simeq \sum_{p=0}^{\infty}\left(-\frac{1}{\omega^2}\right)^{p+1}\langle N\tilde{\mathsf{F}}^{2p+1}N\rangle^{\mathrm{eq}}.$$

*) In fact, contrary to a remark of Lax, Alkemade's treatment is also valid for all orders of ε.

The successive terms can be computed from this; the first two are

$$S_N(\omega) = \frac{2}{\pi\varepsilon}\left[\frac{1}{\omega^2} - \mathrm{e}^{\varepsilon}\left(\frac{\mathrm{e}^{\varepsilon}-1}{\varepsilon}\right)^2 \frac{1}{\omega^4} + \cdots\right], \tag{29}$$

in agreement with (28).

8. *Validity of the Fokker-Planck approximation.* In a short time Δt there is a probability $A\Delta t$ for N to decrease by 1, and a probability $A\,\mathrm{e}^{-\frac{1}{2}\varepsilon-\varepsilon N}\Delta t$ to increase by 1. Thus

$$\lim_{\Delta t\to 0}\frac{\langle \Delta N\rangle_N}{\Delta t} = -A + A\mathrm{e}^{-\frac{1}{2}\varepsilon-\varepsilon N},$$

$$\lim_{\Delta t\to 0}\frac{\langle (\Delta N)^2\rangle_N}{\Delta t} = A + A\mathrm{e}^{-\frac{1}{2}\varepsilon-\varepsilon N}.$$

Hence the Fokker-Planck equation for our problem is

$$\frac{1}{A}\frac{\partial P}{\partial t} = \frac{1}{2}\frac{\partial^2}{\partial N^2}(1+\mathrm{e}^{-\frac{1}{2}\varepsilon-\varepsilon N})P - \frac{\partial}{\partial N}(-1+\mathrm{e}^{-\frac{1}{2}\varepsilon-\varepsilon N})P. \tag{30}$$

It is clear that in this approximation N is to be regarded as a continuous variable. We shall now repeat our previous work for this approximate master equation and compare results.

Firstly one has to find the equilibrium distribution by solving (30) with a zero on the left. The result is

$$P^{\mathrm{eq}}_{\mathrm{FP}} = \frac{1}{Z_{\mathrm{FP}}}\mathrm{e}^{-2\varepsilon N}(1+\mathrm{e}^{-\frac{1}{2}\varepsilon-\varepsilon N})^{-(4/\varepsilon)-1}.$$

This differs materially from the true Gaussian P^{eq} when N is large. However the peak is reproduced more or less correctly, as is seen from the lower moments:

$$\begin{aligned} \varepsilon^{\frac{1}{2}}\langle N\rangle^{\mathrm{eq}}_{\mathrm{FP}} &= O(\varepsilon^{\frac{1}{2}}), \qquad \varepsilon\langle N^2\rangle^{\mathrm{eq}}_{\mathrm{FP}} = 1 + O(\varepsilon^2), \\ \varepsilon^{\frac{3}{2}}\langle N^3\rangle^{\mathrm{eq}}_{\mathrm{FP}} &= O(\varepsilon^{\frac{3}{2}}), \qquad \varepsilon^2\langle N^4\rangle^{\mathrm{eq}}_{\mathrm{FP}} = 3 + O(\varepsilon). \end{aligned} \tag{31}$$

Apart from the terms comprised in the symbol $O(..)$, these are the correct values (compare (11) and (12)).

Secondly, we compute the macroscopic phenomenological equation that results from (30). Clearly from (30) follows

$$\frac{\mathrm{d}}{A\,\mathrm{d}t}\langle N\rangle = \frac{1}{A}\int N\frac{\partial P}{\partial t}\,\mathrm{d}N = -1 + \mathrm{e}^{-\frac{1}{2}\varepsilon}\langle \mathrm{e}^{-\varepsilon N}\rangle.$$

This is identical with the exact expression (14). Going to the limit $\varepsilon \to 0$ *one finds therefore exactly the same macroscopic equation* (15) *as before.*

Thirdly, we compute the fluctuation spectrum. It is easily seen that both (16*a*) and (16*b*) are reproduced exactly in the F–P approximation, but in the equation for the third moment the first two terms are lacking,

$$\frac{\mathrm{d}}{A\,\mathrm{d}t}\langle N^3\rangle = 3\langle N\rangle + 3\mathrm{e}^{-\frac{1}{2}\varepsilon}\langle N\,\mathrm{e}^{-\varepsilon N}\rangle - 3\langle N^2\rangle + 3\,\mathrm{e}^{-\frac{1}{2}\varepsilon}\langle N^2\,\mathrm{e}^{-\varepsilon N}\rangle.$$

However, these two terms did not contribute to (18*c*) anyway, because they are of relative order $\varepsilon^{\frac{1}{2}}$. Consequently, the F–P equation (30) leads to exactly the same formula (21). The only other things required for computing the spectrum were the equilibrium moments (22); as these are reproduced with sufficient accuracy (compare (31)), the conclusion is that *the* F–P *approximation leads to the correct fluctuation spectrum in first order of* ε.

Remark. When comparing the general hypotheses of the various authors with the present calculation, it should be borne in mind that actually this example is rather special. This is exhibited by the fact that there is only one essential parameter in the master equation, namely ε. This parameter serves a dual purpose: on the one hand it measures the validity of the F–P approximation, on the other hand it determines the importance of the non-linear terms. That is the reason why the F–P equation cannot be used beyond the lowest terms in the non-linearity. A similar state of affairs prevails in the case of a heavy particle in a dilute gas (Rayleigh particle)*). Yet there is reason to expect that there exist fundamentally different situations. Both in the case of the diode and of the Rayleigh particle *the non-linearity arises merely from the non-linearity of the Boltzmann factor*. There are other systems in which the non-linearity arises from the actual mechanism that is responsible for the transitions. Examples are the diode with space charge; and the Rayleigh particle, when the non-linear corrections to Stokes' law become important. As soon as the elementary transitions (like the individual jumps of the electrons in the diode, or the separate collisions of the gas molecules with the Rayleigh particle) are no longer statistically uncorrelated, a new non-linearity occurs, which is not due to the Boltzmann factor. Those systems necessarily involve more than one parameter; it may then be possible to manipulate these parameters in such a way as to improve the validity of the F–P approximation without destroying the non-linearity. However, examples of this second kind of non-linearity are probably much harder to calculate explicitly; it is not accidental that so far all models have been of the first kind!

9. *Fluctuations in non-equilibrium states.* In this section we study the fluctuations in states that differ macroscopically from equilibrium. Such

*) Lord Rayleigh, *Scientific Papers* II (Cambridge 1902) p. 473, I am indebted to G. E. Uhlenbeck for drawing my attention to this case, and to A. Siegel for discussions.

states were treated in lowest order in section 4, we shall now find the next order. Clearly an expansion in moments of N is no longer appropriate; instead we shall need the *central* moments. The second central moment for example obeys the equation

$$\frac{\mathrm{d}}{A\,\mathrm{d}t}\{\langle N^2\rangle - \langle N\rangle^2\} = 1 + \mathrm{e}^{-\frac{1}{2}\varepsilon}\,\mathrm{e}^{-\varepsilon N} + 2\mathrm{e}^{-\frac{1}{2}\varepsilon}\,\langle (N - \langle N\rangle)\,\mathrm{e}^{-\varepsilon N}\rangle, \quad (32)$$

which follows directly from (16*a*) and (16*b*). We put

$$\langle (N - \langle N\rangle)^p\rangle = \varepsilon^{-\frac{1}{2}p}\,\mu_p, \qquad (p = 2, 3, \ldots)$$

and suppose μ_p of order 1, in analogy with (17). Thus

$$\langle \mathrm{e}^{-\varepsilon N}\rangle = \mathrm{e}^{-\varepsilon\langle N\rangle}\{1 + \tfrac{1}{2}\varepsilon\mu_2 - \tfrac{1}{6}\varepsilon^{\frac{3}{2}}\mu_3\} + O(\varepsilon^2).$$

Using this expansion one finds for equation (16*a*)

$$\varepsilon\frac{\mathrm{d}\langle N\rangle}{\mathrm{d}\tau} = -1 + \mathrm{e}^{-\varepsilon\langle N\rangle}\{1 - \tfrac{1}{2}\varepsilon + \tfrac{1}{2}\varepsilon\mu_2 - \tfrac{1}{6}\varepsilon^{\frac{3}{2}}\mu_3\} + O(\varepsilon^2), \quad (33a)$$

while (32) gives

$$\frac{\mathrm{d}\mu_2}{\mathrm{d}\tau} = 1 + \mathrm{e}^{-\varepsilon\langle N\rangle}(1 - 2\mu_2 + \varepsilon^{\frac{1}{2}}\mu_3) + O(\varepsilon). \quad (33b)$$

Similarly one finds

$$\frac{\mathrm{d}\mu_3}{\mathrm{d}\tau} = -3\mu_3\,\mathrm{e}^{-\varepsilon\langle N\rangle} + O(\varepsilon^{\frac{1}{2}}). \quad (33c)$$

These equations can again be solved in successive orders of ε. The zeroth order of (33*a*) is of course the macroscopic equation found in section 4; its solution is

$$\varepsilon\langle N\rangle = \log(1 + \mathrm{e}^{\tau_0 - \tau}),$$

where

$$\mathrm{e}^{\tau_0} = \mathrm{e}^{\varepsilon\langle N\rangle_0} - 1.$$

Substitute this in (33*c*) and solve

$$\mu_3(\tau) = \mu_3(0)\left(\frac{1 + \mathrm{e}^{\tau_0}}{\mathrm{e}^{\tau} + \mathrm{e}^{\tau_0}}\right)^3.$$

The factor in parentheses can also be written as

$$1 - \mathrm{e}^{-\varepsilon\langle N\rangle}(1 - \mathrm{e}^{-\tau}); \quad (34)$$

this does not become small until $\varepsilon\langle N\rangle = -eV/kT$ itself is small. Hence μ_3 does not forget its initial value before equilibrium has been reached. For μ_2 one finds to lowest order

$$\mu_2(\tau) = \mu_2(0)\left(\frac{1 + \mathrm{e}^{\tau_0}}{\mathrm{e}^{\tau} + \mathrm{e}^{\tau_0}}\right)^2 + 1 + \frac{\mathrm{e}^{\tau + \tau_0} + (\tau - 1)\,\mathrm{e}^{2\tau_0} - 1 - 3\,\mathrm{e}^{\tau_0}}{(\mathrm{e}^{\tau} + \mathrm{e}^{\tau_0})^2}$$

The coefficient of $\mu_2(0)$ involves again (34); this shows again that *the detailed structure of the initial distribution remains important during the whole process.*

It is of interest to write the next order of $\langle N\rangle$ too:

$$\varepsilon\langle N\rangle = \log(1 + e^{\tau_0-\tau}) - \tfrac{1}{4}\varepsilon\left[\log\frac{1+e^{\tau_0-\tau}}{1+e^{\tau_0}} + \mu_2(\tau) - \mu_2(0)\right].$$

It is here shown explicitly that $\langle N\rangle$ is not a function of τ and N_0 alone, but also depends on $\mu_2(0)$ and on C. Only in the limit $C \to \infty$ does one obtain a well-defined macroscopic equation. This illustrates the argument in section 4.

Of course one is actually interested in a different kind of non-equilibrium states, namely steady states, i.e., states with constant average current. Such states, however, cannot exist in an isolated system, but require an external source or force. It may be questioned, whether it makes sense to speak about fluctuations in the system without taking into account the noise produced by the source. We cannot answer this question definitively, because we here only deal with isolated systems. Yet, the fact that in our non-steady states the details of the initial distribution cannot be neglected, strongly suggests that in the steady states the noise produced by the external source cannot be disregarded either.

Recently Bernard and Callen [6]) have suggested that the approach to equilibrium should be represented by a distribution which at $\tau = 0$ has the form of a shifted equilibrium distribution,

$$P_{\mathrm{BC}}(N_0; N, t) = (2\pi\varepsilon)^{-\frac{1}{2}}\, e^{-\frac{1}{2}\varepsilon(N-N_0)^2}.$$

This corresponds to the initial values

$$\langle N\rangle_0 = N_0, \qquad \mu_2(0) = 1, \qquad \mu_3(0) = 0.$$

Using the equations derived above one finds first

$$\mu_2(\tau) = 1 + \frac{e^{\tau+\tau_0} + \tau e^{2\tau_0} - e^{\tau_0}}{e^{\tau} + e^{\tau_0}},$$

and subsequently

$$\varepsilon\langle N\rangle = \log\,(1 + e^{\tau_0-\tau}) - \tfrac{1}{4}\varepsilon\left[\log\frac{1+e^{\tau_0-\tau}}{1+e^{\tau_0}} + \frac{e^{\tau_0+\tau} + \tau e^{2\tau_0} - e^{\tau_0}}{e^{\tau}+e^{\tau_0}}\right].$$

To first order in N_0 this reduces to

$$\langle N\rangle = N_0\, e^{-\tau} + O(N_0^2) + O(\varepsilon^2).$$

The fact that here the linear law appears is not surprising, because 'first order in N_0' means

$$1 \gg \varepsilon N_0 = eV_0/kT,$$

where V_0 is the average potential at $\tau = 0$.

According to the so-called fluctuation-dissipation theorem the linear term in N_0 is connected with the auto-correlation function by

$$\langle N(0)\, N(\tau)\rangle^{\mathrm{eq}} = \langle N_0 \langle N\rangle_{N_0}\rangle^{\mathrm{eq}} = \langle N_0{}^2\rangle^{\mathrm{eq}}\, \mathrm{e}^{-\tau} = \frac{1}{\varepsilon}\, \mathrm{e}^{-\tau},$$

or

$$\varepsilon\langle N(0)\, N(\tau)\rangle^{\mathrm{eq}} = \mathrm{e}^{-\tau} + O(\varepsilon^2).$$

This disagrees with (23). There are two reasons for this discrepancy. Firstly, it is not correct to use $P_{\mathrm{BC}}(N_0; N, t)$ rather than $P(N_0 \mid N, t)$ for the calculation of the auto-correlation function *). Secondly, in the equilibrium distribution N_0 is itself a quantity of order **) $\varepsilon^{-\frac{1}{2}}$; one cannot therefore go to a linear approximation in N_0 and expect to get the higher terms in ε correctly.

Our conclusion is that *the fluctuation-dissipation theorem is only correct for sufficiently large C, for which the voltage fluctuations are so small that the non-linear terms are unimportant.* In that case the whole problem is linear, and the fluctuation-dissipation theorem reduces to the Nyquist relation.

10. *The fluctuation spectrum to infinite order of* ε. In order to solve the master equation (3) we put

$$P(N, t) = \Psi(N)\, \mathrm{e}^{-\lambda t} = \Psi(N)\, \mathrm{e}^{-(\lambda/\varepsilon)\tau},$$

so that Ψ and λ must satisfy the eigenvalue equation

$$\mathsf{F}\Psi = -\lambda\Psi. \tag{35}$$

The systematic solution of this equation will be published elsewhere; here we shall only verify the result and derive those properties that are needed for calculating the fluctuation spectrum.

The equilibrium distribution (4) provides one solution of (35), to wit

$$\lambda = 0, \qquad \Psi_0(N) = \mathrm{e}^{-\frac{1}{2}\varepsilon N^2 + \eta N}. \tag{36}$$

We now verify by induction that the following eigenvalues and eigenfunctions also satisfy (35),

$$\lambda_n = 1 - \mathrm{e}^{-n\varepsilon}, \quad \Psi_n = \prod_{k=1}^{n} (1 - \mathrm{e}^{-\varepsilon(k-1)}\, \mathsf{E}^{-1})\, \Psi_0. \tag{37}$$

Suppose that for some index $n \geqslant 0$

$$\mathsf{F}\Psi_n = \{\mathsf{E} - 1 + \zeta(\mathsf{E}^{-1} - 1)\, \mathrm{e}^{-\varepsilon N}\}\, \Psi_n = -\lambda_n \Psi_n. \tag{38}$$

*) Because of the non-linearity. In the linear case it makes no difference.

**) Compare equation (17). In the expression for the auto-correlation function the negative powers of ε are, of course, compensated by additional factors ε, as may be seen from the work in section 6.

One then has

$$\begin{aligned}\mathsf{F}\Psi_{n+1} &= \mathsf{F}(1 - \mathrm{e}^{-\varepsilon n}\mathsf{E}^{-1})\,\Psi_n \\ &= (1 - \mathrm{e}^{-\varepsilon n}\mathsf{E}^{-1})\,\mathsf{F}\Psi_n - \mathrm{e}^{-\varepsilon n}[\mathsf{F}, \mathsf{E}^{-1}]\,\Psi_n.\end{aligned}$$

The commutator of F and E^{-1} is

$$\begin{aligned}[\mathsf{F}, \mathsf{E}^{-1}] &= \zeta(\mathsf{E}^{-1} - 1)(\mathrm{e}^{-\varepsilon N}\,\mathsf{E}^{-1} - \mathsf{E}^{-1}\,\mathrm{e}^{-\varepsilon N}) \\ &= \zeta(\mathsf{E}^{-1} - 1)\,\mathsf{E}^{-1}(\mathrm{e}^{-\varepsilon} - 1)\,\mathrm{e}^{-\varepsilon N}.\end{aligned}$$

Hence

$$\begin{aligned}\mathsf{F}\Psi_{n+1} &= -\lambda_n(1 - \mathrm{e}^{-\varepsilon n}\,\mathsf{E}^{-1})\,\Psi_n \\ &= -\mathrm{e}^{-\varepsilon n}(\mathrm{e}^{-\varepsilon} - 1)\,\mathsf{E}^{-1}\{\zeta(\mathsf{E}^{-1} - 1)\,\mathrm{e}^{-\varepsilon N}\,\Psi_n\}.\end{aligned}$$

For the quantity $\{\ \}$ we substitute from (38):

$$\begin{aligned}\mathsf{F}\Psi_{n+1} &= -\lambda_n\Psi_{n+1} - \mathrm{e}^{-\varepsilon n}(\mathrm{e}^{-\varepsilon} - 1)\,\mathsf{E}^{-1}\,(-\lambda_n - \mathsf{E} + 1)\,\Psi_n \\ &= (\mathrm{e}^{-\varepsilon n} - 1)\,\Psi_{n+1} - \mathrm{e}^{-\varepsilon n}(\mathrm{e}^{-\varepsilon} - 1)(\mathrm{e}^{-\varepsilon n}\,\mathsf{E}^{-1} - 1)\,\Psi_n \\ &= (\mathrm{e}^{-\varepsilon n} - 1 + \mathrm{e}^{-\varepsilon(n+1)} - \mathrm{e}^{-\varepsilon n})\,\Psi_{n+1} \\ &= -\lambda_{n+1}\,\Psi_{n+1}. \qquad \text{q.e.d.}\end{aligned}$$

For example,

$$\begin{aligned}\Psi_1 &= \Psi_0\{1 - \mathrm{e}^{\varepsilon N - \eta - \frac{1}{2}\varepsilon}\}, \\ \Psi_2 &= \Psi_0\{1 - (1 + \mathrm{e}^{-\varepsilon})\,\mathrm{e}^{\varepsilon N - \eta - \frac{1}{2}\varepsilon} + \mathrm{e}^{2\varepsilon N - 2\eta - 3\varepsilon}\}.\end{aligned}$$

One easily sees that in general

$$\Phi_n = \Psi_n/\Psi_0 \text{ is a polynomial of degree } n \text{ in } \mathrm{e}^{\varepsilon N}.$$

The term with the highest power of $\mathrm{e}^{\varepsilon N}$ is obtained by taking the highest possible power of E^{-1} in (37):

$$\begin{aligned}\frac{1}{\Psi_0}\prod_{k=1}^{n}(-\mathrm{e}^{-\varepsilon(k-1)}\,\mathsf{E}^{-1})\,\Psi_0 &= (-1)^n\,\mathrm{e}^{-\frac{1}{2}\varepsilon n(n-1)}\,\frac{\Psi_0(N-n)}{\Psi_0(N)} \\ &= (-1)^n\,\mathrm{e}^{-\varepsilon n^2 + \frac{1}{2}\varepsilon n - \eta n}\,\mathrm{e}^{\varepsilon N n}. \qquad (39)\end{aligned}$$

We now prove the following *orthogonality and normalization* property,

$$\mathsf{S}\Phi_m\Psi_n = \mathsf{S}\frac{\Psi_m\Psi_n}{\Psi_0} = \delta_{mn}\,Z\,\mathrm{e}^{\varepsilon n}\prod_{k=1}^{n}(1 - \mathrm{e}^{-\varepsilon k}). \qquad (40)$$

According to (37) the left-hand side is also

$$\mathsf{S}\Phi_m\prod_{k=1}^{n}(1 - \mathrm{e}^{-\varepsilon(k-1)}\,\mathsf{E}^{-1})\,\Psi_0 = \mathsf{S}\Psi_0\prod_{k=1}^{n}(1 - \mathrm{e}^{-\varepsilon(k-1)}\,\mathsf{E})\Phi_m. \qquad (41)$$

Take an arbitrary term $\mathrm{e}^{\varepsilon N p}$ of Φ_m; one easily sees

$$\prod_{k=1}^{n}(1 - \mathrm{e}^{-\varepsilon(k-1)}\,\mathsf{E})\,\mathrm{e}^{\varepsilon N p} = \mathrm{e}^{\varepsilon N p}\prod_{k=1}^{n}(1 - \mathrm{e}^{-\varepsilon(k-1-p)}).$$

For each $p < n$ this product contains a factor zero. Hence (41) vanishes if $m < n$. If $m > n$ the left-hand side of (4) also vanishes because it is symmetric in m and n. Finally for $m = n$ just one term of Φ_n survives in (41), namely the highest one, which has been calculated in (39). By some algebraic manipulations one then finds (40).

For $n = 0$, (40) reduces to the definition (5) of Z. We shall define *normalized eigenfunctions* $\overline{\Psi}_n$ as follows

$$\overline{\Psi}_0 = Z^{-1}\Psi_0 = P^{\mathrm{eq}},$$

$$\overline{\Psi}_n = Z^{-1}\left[\mathrm{e}^{\varepsilon n}\prod_{k=1}^{n}(1-\mathrm{e}^{-\varepsilon n})\right]^{-\frac{1}{2}}\Psi_n, \tag{42}$$

so that

$$\mathsf{S}\overline{\Psi}_m\overline{\Psi}_n/\overline{\Psi}_0 = \delta_{mn}.$$

Once the eigenvalues and eigenfunctions of the master equation are known, the fluctuation spectrum can be found from the relation *)

$$S_N(\omega) = \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{\lambda_n/\varepsilon}{(\lambda_n/\varepsilon)^2+\omega^2}[\mathsf{S}N\overline{\Psi}_n(N)]^2. \tag{43}$$

In order to compute the coefficient [ ] write

$$\begin{aligned}\mathsf{S}N\Psi_n &= \mathsf{S}\Psi_{n-1}(1-\mathrm{e}^{-\varepsilon(n-1)}\mathsf{E})N\\ &= (1-\mathrm{e}^{-\varepsilon(n-1)})\,\mathsf{S}N\Psi_{n-1} - \mathrm{e}^{-\varepsilon(n-1)}\,\mathsf{S}\Psi_{n-1}.\end{aligned}$$

For the last term the orthonormality property (40) yields

$$\mathsf{S}\Psi_{n-1} = \mathsf{S}\Phi_0\Psi_{n-1} = \delta_{n,1}Z.$$

Hence for $n > 1$ only the first term survives, giving rise to a recurrence relation, with the result

$$\mathsf{S}N\Psi_n = \prod_{k=1}^{n-1}(1-\mathrm{e}^{-\varepsilon k})\,\mathsf{S}N\Psi_1 = -Z\prod_{k=1}^{n-1}(1-\mathrm{e}^{-\varepsilon k}).$$

Substituting in (43) while remembering the normalization (42)

$$S_N(\omega) = \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{\lambda_n/\varepsilon}{(\lambda_n/\varepsilon)^2+\omega^2}\,\frac{\prod_{k=1}^{n-1}(1-\mathrm{e}^{-\varepsilon k})^2}{\mathrm{e}^{\varepsilon n}\prod_{k=1}^{n}(1-\mathrm{e}^{-\varepsilon k})},$$

or, using the explicit value for λ_n,

$$S_N(\omega) = \frac{2}{\pi\varepsilon}\sum_{n=1}^{\infty}\frac{\mathrm{e}^{-\varepsilon n}}{\left(\dfrac{1-\mathrm{e}^{-\varepsilon n}}{\varepsilon}\right)^2+\omega^2}\prod_{k=1}^{n-1}(1-\mathrm{e}^{-\varepsilon k}). \tag{44}$$

*) See reference [3]. We here write λ_n/ε rather than λ_n, because we want to use τ as time variable in order to compare the result with section 6.

Thus we find for $S_N(\omega)$ an analytic function of ω of the type anticipated in (27). The poles are for low n approximately given by

$$\pm i\lambda_n/\varepsilon = \pm i\,[n - \tfrac{1}{2}\varepsilon n^2 + \tfrac{1}{6}\varepsilon^2 n^3 - \ldots].$$

For $n = 1$ the first term of this series agrees with (26). For high n the poles accumulate towards $\pm i/\varepsilon$, a feature that could not have been found by the expansion method. The first two of the coefficients in the numerators,

$$c_1 = \mathrm{e}^{-\varepsilon} = 1 - \varepsilon + \tfrac{1}{2}\varepsilon^2 + \ldots$$

$$c_2 = \mathrm{e}^{-2\varepsilon}(1 - \mathrm{e}^{-\varepsilon}) = \varepsilon - 2\varepsilon^2 + \ldots$$

also agree with (26).

For the high frequency limit (44) yields

$$S_N(\omega) \simeq \frac{2}{\pi\varepsilon}\frac{X}{\omega^2}, \qquad X = \sum_{n=1}^{\infty} \mathrm{e}^{-\varepsilon n} \prod_{k=1}^{n-1} (1 - \mathrm{e}^{-\varepsilon k}).$$

This is in disagreement with (29), inasmuch as X is not identically equal to 1. Yet it should be noted that if X is expanded formally in ε one finds that all terms but the first one vanish,

$$X = 1 + 0\cdot\varepsilon + 0\cdot\varepsilon^2 + \ldots.$$

This shows that the discrepancy consists of terms that are not analytic in ε, and are small of infinite order of ε.

The reason why (44) is not rigorously correct is that when using (43) we have tacitly assumed the eigenfunctions Ψ_n to be complete. This turns out to be incorrect: there exist other eigenfunctions with eigenvalues

$$\lambda_n' = 1 + \zeta\,\mathrm{e}^{-\varepsilon n}. \qquad (-\infty < n < +\infty)$$

They give rise to additional terms in (44), which I have not yet been able to compute. It is interesting to note that the λ_n accumulate towards 1 from below, whereas the λ_n' accumulate towards 1 from above. This shows that the spectrum of relaxation times consists of two regions, separated by a discontinuity at

$$\varepsilon R_0 C = e^2 R_0/kT. \tag{45}$$

The relaxation times below this dividing point contribute to the spectrum only terms whose expansions in ε vanish in all orders. In other words, (44) is the result one would get by solving the master equation in successive orders of ε and computing *all* orders, but it does not contain those terms that cannot be expanded in ε. Hence we were justified in comparing the successive orders of (44) with (26). Moreover, in all practical cases the discrepancy will be extremely small.

The dividing point (45) between both regions of the spectrum of relaxation times is equal to $1/A$, that is, the average time interval between two electron

jumps from electrode 1 to 2 (or vice versa). The reason why this quantity shows up so conspicuously in the spectrum may be roughly understood as follows. The electrons are treated as almost entirely independent of each other; they only influence each other's transition probability through the voltage. The fluctuations with frequencies $\omega \ll A$ (i.e., with periods much greater than $1/A$) are statistical fluctuations involving a large number of electrons. They would give rise to a mean square charge on the condenser increasing linearly with time, if they were not kept in check by the simultaneous increase of the potential. Hence they have relaxation times proportional to C, like the RC-time itself. This is for instance exhibited by the expression for $S_I(f)$ given in section 6. These fluctuations may be regarded as a *modification of the macroscopic picture of an electric fluid, arising from the discreteness of the charge carriers.* On the other hand, the fluctuations with frequencies $\omega \gg A$ only involve individual electron transitions; their relaxation times $(\lambda_n' A)^{-1}$ are therefore much less sensitive to C. These fluctuations may be regarded as a *modification of the microscopic picture of independent particles, arising from their interaction through the macroscopic* V. Yet this rough explanation does not make clear why there should be such a sharp dividing line between both types of behaviour.

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REFERENCES

1) MacDonald, D. K. C., Phil. Mag. **45** (1954) 63.
2) MacDonald, D. K. C., Phys. Rev. **108** (1957) 541.
3) Van Kampen, N. G., Phys. Rev. **110** (1958) 319.
4) Alkemade, C. T. J., Physica **24** (1958) 1029.
5) Lax, M., Revs. Mod. Phys. **32** (1960) 25.
6) Bernard, W. and Callen, H. B., Revs. Mod. Phys. **31** (1959) 1017
7) Marek, A., Physica **25** (1959) 1358.