

# Fluctuations in Nonlinear Systems

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## 1 Introductory Section

### 1.1 Introduction

*Thermodynamics* deals with macroscopic quantities (such as density, energy, pressure) and ascribes well-defined values to them. This is only an approximation, since matter is not really continuous, but consists of discrete particles. The approximate nature is exhibited by the existence of fluctuations. *Classical statistical mechanics* enables one to compute the mean square of the deviations from the thermodynamical values in the equilibrium state. However, we are interested in *time-dependent fluctuations* (also called noise, or Brownian movement in a generalized sense); that is, we want to know how the deviations at different times are correlated with each other. Since the dimension time enters, this problem is outside the scope of equilibrium statistical mechanics, and belongs to the statistical mechanics of nonequilibrium processes. Yet the earlier treatments, like Langevin's treatment of Brownian movement, were able to short-cut the general theory of nonequilibrium processes, by means of an inspired guess. This short cut has turned out to be only possible for systems with a linear response; in Section 1.3 it will be shown how the attempts to do the same for nonlinear systems have failed. To find a reliable starting point for the theory of nonlinear fluctuations we shall therefore have to go back to the general theory (Section 3).

In order to define what is meant by *nonlinear fluctuations*, consider the simple electric circuit of Fig. 1, consisting of a condenser  $C$ , and a dissipative element  $R$ , which is in thermal equilibrium with a heat bath at temperature  $T$ . If the resistance  $R$  is constant, *i.e.*, independent of the current, the  $I - V$  characteristic is given by Ohm's law, so that the response of the resistor to an impressed potential difference  $V$  is linear. To put it differently, the charge  $Q$  on the condenser obeys a linear differential equation

$$\frac{dQ}{dt} = -\frac{V}{R} = -\frac{Q}{RC}. \quad (1)$$

In this case, the fluctuations in the current, or in the charge, are called *linear* fluctuations, and may be treated by the standard linear noise theory.

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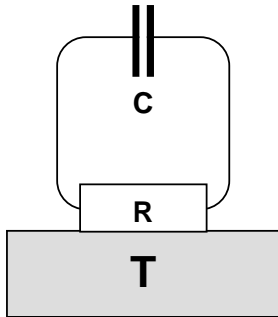


Figure 1: **MacDonald's circuit.**

Of course, in Eq. 1 the fluctuations have been neglected: this equation is valid only on a macroscopic, thermodynamic level. For definiteness we shall call such equations “*phenomenological laws*” (without implying that no other phenomena can be observed).

If, on the other hand, the dissipative element consists of a semiconductor, the  $I - V$  characteristic may well be nonlinear. This can be described by allowing  $R$  to depend on  $V$ . It is more convenient to use the conductivity  $G(V) = 1/R(V)$ , so that  $Q$  now obeys the *nonlinear phenomenological law*

$$\frac{dQ}{dt} = -\frac{Q}{C} G\left(\frac{Q}{C}\right). \quad (2)$$

Yet, even in this case the linear noise theory is a very good approximation because the fluctuations are normally so small that  $V \cdot G(V)$  may be regarded as linear in the range of  $V$  that is covered by them (Fig. 2). However, the theory of nonlinear fluctuations goes beyond this approximation, and studies the effect of the curvature of the characteristic on the fluctuations.

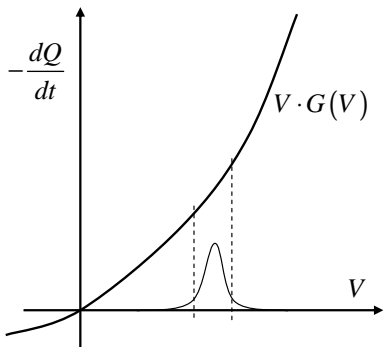


Figure 2: **Nonlinear response and its effect on fluctuations.**

It should be emphasized that this problem is different from the purely mathematical one of noise with known statistical properties passing through a nonlinear device (Middleton, 1951; Deutsch, 1962). It is also different from Brownian movement in an external, nonlinear field of force (Kramers, 1940; Rytov, 1955; Brinkman, 1957, 1958). In our case the dissipative element, which produces the noise, is itself nonlinear, and one has to find the statistical properties of the noise it produces. This is essentially a physical problem belonging to nonequilibrium statistical mechanics. We shall only study the case of one variable. Accordingly, we do not discuss the closely related problem of Onsager relations for nonlinear systems (van Kampen, 1957; Uhlhorn, 1960; Stratonovich, 1960).

## 1.2 Linear Fluctuation Theory

This section briefly reviews the linear theory, insofar as it is needed for later work.

Let  $Q$  be a physical quantity obeying a *linear phenomenological law*

$$\dot{Q} = -\gamma_0 Q, \quad (3)$$

$\gamma_0$  being a constant. For example,  $Q$  may be the charge on a condenser in Fig. 1, with  $\gamma_0 = 1/RC$ . Or  $Q$  may be one velocity component of a heavy particle suspended in a gas or liquid. In order to describe also the fluctuations, one writes for the precise, *microscopic* value  $q$  of the same physical quantity the Langevin equation

$$\dot{q} = -\gamma_0 q + \kappa(t). \quad (4)$$

This equation is only meaningful if some information about the “random force”  $\kappa(t)$  is added. Since  $\kappa(t)$  is pictured as a very rapidly and irregularly varying function of time, it can only be described by its stochastic properties. Specifically one assumes

$$\langle \kappa(t) \rangle = 0, \quad (5)$$

where  $\langle \rangle$  denotes the average over a time interval long compared to the rapid variations in  $\kappa(t)$ , but short compared to the phenomenological damping time  $1/\gamma_0$ . It is often convenient to visualize it as an ensemble average. In addition one assumes

$$\langle \kappa(t)\kappa(t') \rangle = \Gamma \delta(t - t'), \quad (6)$$

where  $\Gamma$  is a constant independent of  $t$  and  $q$ . The delta-function is actually a sharply peaked but finite function, whose width is the autocorrelation time of  $\kappa(t)$ . These assumptions about  $\kappa(t)$  constitute the

short cut replacing the general theory of nonequilibrium processes.

From Eqs. 4 and 5 it follows immediately that  $\langle q \rangle$  satisfies the phenomenological law (3), and may therefore be identified with the macroscopic  $Q$ . This identification being made, it may be concluded that Eq. 4 correctly describes the phenomenology of the system in or outside equilibrium.

In equilibrium, one has  $Q = 0$  according to Eq. 3. Hence also  $\langle q \rangle = 0$ , but  $q$  will be a fluctuating function of  $t$ . Its principal stochastic properties are described by the *autocorrelation function*

$$\langle q(0)q(t) \rangle^{eq} \equiv \langle q(0)\langle q(t) \rangle_{q(0)} \rangle^{eq}. \quad (7)$$

This notation is meant to indicate the following definition: Take a certain value  $q(0)$  at  $t = 0$ , calculate the average  $\langle q(t) \rangle_{q(0)}$  conditional on the given value  $q(0)$ , multiply this conditional average by  $q(0)$ , and finally average this product over all values  $q(0)$  as they occur in the equilibrium distribution. One readily finds from Eq. 4 using Eq. 5

$$\langle q(t) \rangle_{q(0)} = q(0)e^{-\gamma_0 t}, \quad (8)$$

so that the autocorrelation function is found to be

$$\langle q(0)q(t) \rangle^{eq} = \langle q^2 \rangle^{eq} e^{-\gamma_0 t}. \quad (9)$$

$\langle q^2 \rangle^{eq}$  is determined by equilibrium statistical mechanics (law of equipartition) and will therefore be regarded as a known quantity. Thus we have found the autocorrelation function, even without using assumption (6).

The *spectral density of fluctuations*, or briefly *fluctuation spectrum*,  $S_q(\omega)$ , is, according to the theorem of Wiener-Khintchine, equal to the Fourier transform of the autocorrelation function<sup>1</sup>

$$S_q(\omega) = \frac{2}{\pi} \int_0^\infty \langle q(0)q(t) \rangle^{eq} \cos \omega t \, dt. \quad (10)$$

This fluctuation spectrum is the quantity usually measured. For the present linear case one finds using Eq. 9

$$S_q(\omega) = \frac{2}{\pi} \langle q^2 \rangle^{eq} \frac{\gamma_0}{\gamma_0^2 + \omega^2}. \quad (11)$$

In the case of an electric circuit, like in Fig. 1, one is more interested in the fluctuation spectrum for the

<sup>1</sup>Note that we write the spectrum in terms of the circular frequency  $\omega$ ; expressed in the conventional frequency scale it is  $S_q(f) = 2\pi S_q(\omega)$ .

current  $\dot{q}$ , which differs from  $S_q(\omega)$  only by a factor  $\omega^2$ ,

$$S_{\dot{q}}(\omega) = \frac{2}{\pi} kTC\gamma_0 \frac{(\omega/\gamma_0)^2}{1 + (\omega/\gamma_0)^2}. \quad (12)$$

In the limit of high frequencies

$$S_{\dot{q}}(\omega) = \omega^2 S_q(\omega) \rightarrow (2/\pi)(kT/R), \quad (\omega \gg 1/RC). \quad (13)$$

It will be shown in Section 3.2 that this high-frequency limit remains valid in the nonlinear case, provided one takes for  $R$  the resistance at  $V = 0$ .

An alternative approach in linear noise theory consists in describing the stochastic properties of  $q(t)$  by means of the probability distribution  $P(q, t)$  rather than by the moments. It is then asserted that  $P(q, t)$  obeys the ‘‘linear Fokker-Planck equation’’ (Fokker, 1913, 1914; Planck, 1917)

$$\frac{\partial P}{\partial t} = \gamma_0 \frac{\partial}{\partial q} qP + \frac{\Gamma}{2} \frac{\partial^2 P}{\partial q^2}. \quad (14)$$

It is readily verified that this leads to the same equations for  $\langle q(t) \rangle$  and  $\langle q^2(t) \rangle$  as the Langevin equation.<sup>2</sup> In addition the F-P equation (14) has one time-independent solution, which is a Gaussian and may therefore be identified with the equilibrium distribution of  $q$ . Yet we shall see that in the nonlinear case the F-P equation is only a first approximation.

### 1.3 Early History

In this section a number of earlier papers are reviewed, which serves the purpose of pointing out the difficulties and formulating the problems that are summarized in Section 1.4. The reader who is only interested in the present state of the theory may skip this section.

After a casual remark by Kramers (Kramers, 1940), MacDonald (MacDonald, 1954) was the first to clearly state the problem of fluctuations produced by a dissipative element with nonlinear response. He studied as a special example the electric circuit of Fig. 1,  $R$  being an element obeying the phenomenological law (2). He then introduced as a ‘‘general hypothesis’’: the average of the microscopic variable  $q$  obeys the phenomenological law,

$$\frac{d}{dt} \langle q \rangle = -\frac{\langle q \rangle}{C} G \left( \frac{\langle q \rangle}{C} \right). \quad (15)$$

<sup>2</sup>See also the discussion in Section 3.6, particularly footnote 13.

In particular he took as a simple example of a nonlinear (but symmetrical) conductance function<sup>3</sup>  $G$

$$(1/C) G(Q/C) = \gamma_0 + \gamma_2 Q^2. \quad (16)$$

Then, by applying Eq. 15 to an ensemble with specified  $q(0)$ , one obtains  $\langle q(t) \rangle_{q(0)}$ ; this leads to the autocorrelation function and thence to the fluctuation spectrum for the current. The result is, to first order in  $\gamma_2$ , putting  $\gamma'' = kTC\gamma_2/\gamma_0$ ,

$$S_{\dot{q}}(\omega) = \frac{2}{\pi} kTC\gamma_0 \times \left[ \left(1 - \frac{3}{2} \gamma''\right) \frac{(\omega/\gamma_0)^2}{1 + (\omega/\gamma_0)^2} + \frac{1}{2} \gamma'' \frac{(\omega/\gamma_0)^2}{1 + (\omega/3\gamma_0)^2} \right]. \quad (17)$$

For  $\gamma_2 = 0$  this reduces of course to Eq. 12. The nonlinearity in the phenomenological law gives rise to an extra term in the spectrum corresponding to a relaxation time  $1/3\gamma_0$ . Note that the high frequency limit differs from the linear one, Eq. 13.

In addition to the case (16), MacDonald studied, as an example of an asymmetrical phenomenological law, the idealized rectifier:

$$G(Q/C) = \begin{cases} C\beta_1, & Q > 0 \\ C\beta_2, & Q < 0 \end{cases}. \quad (18)$$

This yields the fluctuation spectrum

$$S_{\dot{q}}(\omega) = \frac{2}{\pi} kTC \left[ \frac{\beta_1}{2} \frac{(\omega/\beta_1)^2}{1 + (\omega/\beta_1)^2} + \frac{\beta_2}{2} \frac{(\omega/\beta_2)^2}{1 + (\omega/\beta_2)^2} \right].$$

Polder (Polder, 1954) criticized MacDonald's "general hypothesis" (15). Consider an ensemble of  $N$  idealized rectifiers obeying Eq. 18, all having the same charge  $q(0)$  at  $t = 0$ . Let  $q(0)$  be positive; then by Eq. 15 for all  $t > 0$

$$\langle q(t) \rangle = q(0)e^{-\beta_1 t}. \quad (19)$$

On the other hand, select an arbitrary  $t_1 > 0$ . The individual values of  $q(t_1)$  are spread around  $\langle q(t_1) \rangle$ , and some of them will be negative. Decompose the ensemble into subensemble  $I$ , consisting of all  $N_I$  rectifiers with  $q(t_1) > 0$ ; and subensemble  $II$  consisting of all  $N_{II}$  rectifiers with  $q(t_1) < 0$ . One then finds for  $t > t_1$ ,

$$\langle q(t) \rangle = (N_I/N) \langle q(t_1) \rangle_I e^{-\beta_1(t-t_1)} + (N_{II}/N) \langle q(t_1) \rangle_{II} e^{-\beta_2(t-t_1)},$$

<sup>3</sup>MacDonald writes  $\alpha/C$ ,  $\gamma/C$ , where we have set  $\gamma_0$ ,  $\gamma_2$ . For consistency we shall sometimes alter the notation of the original authors, without explicitly mentioning it.

which is incompatible with Eq. 19. Thus Polder showed that Eq. 15 is inconsistent with the concept of  $q(t)$  as a random function.

As an alternative, Polder suggested an equation for the probability distribution  $P(q, t)$ , viz.

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial q} \left[ G \left( \frac{q}{C} \right) \left\{ \frac{q}{C} P + kT \frac{\partial P}{\partial q} \right\} \right]. \quad (20)$$

This is a nonlinear generalization of the linear Fokker-Planck equation (14). Moreover Eq. 20 yields the correct Gaussian equilibrium distribution, but it gives instead of Eq. 15,

$$\frac{d}{dt} = - \left\langle \frac{q}{C} G(q) \right\rangle + kT \left\langle \frac{d}{dq} G(q) \right\rangle. \quad (21)$$

Only for the linear case,  $G = \text{constant}$ , does this coincide with (15). We shall presently develop the consequences of Eq. 20.

In a second paper, MacDonald (1957) defines a function  $\tilde{G}(q)$  by taking a subensemble with specified value  $q = q_0$  and setting

$$\langle \dot{q} \rangle_{q_0} = -q_0 \tilde{G}(q_0)/C. \quad (22)$$

There is of course no inconsistency in this, and  $\tilde{G}(q_0)$  coincides with the phenomenological  $G(q_0/C)$  when fluctuations are neglected. On the other hand, Eq. 22 does not provide a means for finding  $\langle q \rangle$  as a function of  $t$ . It is then argued that the probability distribution  $P(q, t)$  must obey

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial q} \left[ \frac{q}{C} \tilde{G}(q) P + kT \frac{\partial}{\partial q} \tilde{F}(q) P \right]. \quad (23)$$

This is again a nonlinear generalization of the F-P equation (14), more general than Polder's generalization (20) because of the as yet unknown function  $\tilde{F}(q)$ .  $\tilde{F}(q)$  could be determined if  $P^{eq}(q)$  were known, but MacDonald questions the validity of the Gaussian distribution

$$P^{eq}(q) = (2\pi kTC)^{-\frac{1}{2}} \exp \left[ -\frac{q^2}{kTC} \right] \quad (24)$$

in the presence of nonlinearity. He does not doubt the validity of  $\langle q^2 \rangle^{eq} = kTC$ , since this can be derived from the second law of thermodynamics by the same argument that Nyquist (1928) used. This leads to a condition on  $\tilde{F}$ ,

$$\langle \tilde{F}(q) \rangle^{eq} = \langle q^2 \tilde{G}(q) \rangle^{eq} / \langle q^2 \rangle^{eq}. \quad (25)$$

This relation is sufficient information about  $\tilde{F}$  to obtain the fluctuation spectrum in the particular case

$$(1/C)\tilde{G}(q) = \tilde{\gamma}_0 + \tilde{\gamma}_2 q^2. \quad (26)$$

One finds to first order in  $\tilde{\gamma}_2$ , putting  $\tilde{\gamma}'' = kTC\tilde{\gamma}_2/\tilde{\gamma}_0$ ,

$$S_{\dot{q}}(\omega) = \frac{2}{\pi} kTC\tilde{\gamma}_0 (1 + 3\tilde{\gamma}'') \frac{(\omega/\tilde{\gamma}_0)^2}{(1 + 3\tilde{\gamma}'') + (\omega/\tilde{\gamma}_0)^2}. \quad (27)$$

In contrast to Eq. 17, one does not now find an extra term with one-third of the relaxation time, but instead the original relaxation is slightly shifted. We shall show in Section 2.2 that in the correct formula both effects are present. The high-frequency limit is again different from Eq. 13.

It should be remarked, however, that one cannot identify  $\tilde{\gamma}_0, \tilde{\gamma}_2$  with the coefficients  $\gamma_0, \gamma_2$  of the phenomenological response. This is demonstrated by noting that Eq. 22 yields for an arbitrary ensemble

$$\begin{aligned} \langle \dot{q} \rangle &= -\langle q\tilde{G}(q) \rangle / C \quad (28) \\ &= -\frac{\langle q \rangle}{C} \tilde{G}(\langle q \rangle) - \frac{\langle (q - \langle q \rangle)^2 \rangle}{2C} \frac{d^2}{d\langle q \rangle^2} \langle q \rangle \tilde{G}(\langle q \rangle) - \dots \end{aligned}$$

Obviously this cannot be identified with the phenomenological equation (2), because there are additional terms depending on the fluctuations.

As a second example, MacDonald studies a model for the metal-oxide rectifying contact discussed by Mott and Gurney (1940). The phenomenological law is

$$\frac{dQ}{dt} = -\frac{Q}{C} G\left(\frac{Q}{C}\right) = I_0(1 - e^{eQ/kTC}), \quad (29)$$

where  $I_0$  is a constant and  $-e$  the electron charge. Identifying  $\tilde{G}$  with  $G$  he writes

$$\begin{aligned} \frac{1}{C}\tilde{G}(q) &= \frac{I_0 e}{kTC} + \frac{I_0}{2} \left(\frac{e}{kTC}\right)^2 q + \frac{I_0}{6} \left(\frac{e}{kTC}\right)^3 q^2 \\ &= \tilde{\gamma}_0 + \tilde{\gamma}_1 q + \tilde{\gamma}_2 q^2. \quad (30) \end{aligned}$$

A consequence from this is that, since  $\langle \dot{q} \rangle^{eq}$  must vanish,

$$\langle q \rangle^{eq} = -(\tilde{\gamma}_1/\tilde{\gamma}_0)\langle q^2 \rangle^{eq} = -\frac{1}{2} e. \quad (31)$$

This anomalous result was also obtained by Alkemade (1958) and Lax (1960). Marek (1959) showed that it is incompatible with the second law of thermodynamics (see, however, Section 2.2). The same problem had been studied by Brillouin (1950); he added a small

constant emf to the right-hand side of Eq. 29 such as to cancel the  $-\frac{1}{2} e$  in Eq. 31. It is shown in Section 2.2 that such a constant emf does indeed exist, but only in the microscopic equation (22); it does not show up in the phenomenological law (29).

No further results can be obtained unless more is known about  $\tilde{F}(q)$ . MacDonald makes the ‘‘plausible assumption’’  $\tilde{F}(q) = \text{constant} = \bar{F}$ , where  $\bar{F}$  is determined by Eq. 25. It is then possible to find the fluctuation spectrum from Eq. 23. Putting  $\varepsilon = e^2/kTC$  one finds

$$S_{\dot{q}}(\omega) = \frac{2}{\pi} kTC\tilde{\gamma}_0 \times \left[ \left(1 - \frac{7}{4} \varepsilon\right) \frac{(\omega/\tilde{\gamma}_0)^2}{(1 + \varepsilon)^2 + (\omega/\tilde{\gamma}_0)^2} + \frac{\varepsilon}{4} \frac{(\omega/\tilde{\gamma}_0)^2}{1 + (\omega/2\tilde{\gamma}_0)^2} \right]. \quad (32)$$

Van Kampen (1958) developed the consequences of the nonlinear F-P equation

$$\frac{\partial P(q, t)}{\partial t} = kT \frac{\partial}{\partial q} \left\{ G\left(\frac{q}{C}\right) P^{eq}(q) \frac{\partial P(q, t)}{\partial q} \right\}, \quad (33)$$

in which  $P^{eq}$  was supposed to be Gaussian, Eq. 24, so that Eq. 33 is identical with Polder’s equation (20). A systematic perturbation expansion yields, in the case defined by Eq. 16, for the fluctuation spectrum to second order in  $\gamma'' \equiv kTC\gamma_2/\gamma_0$

$$S_{\dot{q}}(\omega) = \frac{2}{\pi} kTC\tilde{\gamma}_0 \times \left[ \left\{ 1 + \gamma'' - \frac{9}{2} \gamma''^2 \right\} \frac{(\omega/\tilde{\gamma}_0)^2}{(1 + \gamma'' - 3\gamma''^2)^2 + (\omega/\tilde{\gamma}_0)^2} + \frac{\gamma''^2}{2} \frac{(\omega/\tilde{\gamma}_0)^2}{1 + (\omega/3\tilde{\gamma}_0)^2} \right]; \quad (34)$$

and for the case  $(1/C)G(Q/C) = \gamma_0 + \gamma_1 Q$ , to second order in  $\gamma' \equiv \sqrt{kTC}\gamma_1/\gamma_0$ ,

$$S_{\dot{q}}(\omega) = \frac{2}{\pi} kTC\tilde{\gamma}_0 \times \left[ \frac{(1 - 2\gamma'^2)^2 (\omega/\tilde{\gamma}_0)^2}{(1 - 2\gamma'^2)^2 + (\omega/\tilde{\gamma}_0)^2} + \gamma'^2 \frac{(\omega/\tilde{\gamma}_0)^2}{1 + (\omega/2\tilde{\gamma}_0)^2} \right].$$

Davies (1958), using the same expansion method, developed the consequences of Eq. 23 of MacDonald, but he also assumed  $P^{eq}$  to be Gaussian, Eq. 24, so that  $\tilde{F}$  and  $\tilde{G}$  are connected by

$$\tilde{G}(q) = \tilde{F}(q) - \frac{kTC}{q} \frac{d\tilde{F}(q)}{dq}.$$

He then found for the fluctuation spectrum in the case defined by Eq. 26 the same result (27) that MacDonald found.

The fact that this calculation, although practically identical with that of van Kampen, yields a different result pinpoints the reason for the discrepancy between Eqs. 27 and 34: the two nonlinear F-P equations (23) and (33) do *not* become identical on identifying  $\tilde{G}(q)$  with  $G(q)$ . This is exhibited by the difference between Eqs. 28 and 21.<sup>4</sup> As both treatments are equally legal and plausible generalizations of the linear case, it cannot be decided at this point whether  $\tilde{G}$  or  $G$  is to be identified with the nonlinear phenomenological damping law. In fact, it will be shown that neither is correct, because *one cannot describe the nonlinear case by a F-P equation or any other second order differential equation for  $P(q, t)$ .*

Lax (1960) noticed the difference of MacDonald-Davies v. Polder-van Kampen, but regarded the former standpoint as self-evident. However, he went beyond the F-P approximation, using the full expansion

$$\frac{\partial P}{\partial t} = \sum_{n=1}^{\infty} \left( -\frac{\partial}{\partial q} \right)^n D_n(q)P \quad (35)$$

(“Kramers-Moyal expansion”; Kramers, 1940; Moyal, 1949). The functions  $D_n(q)$  are unknown, except  $D_1(q)$  which is identified with the phenomenological function  $-(Q/C)G(Q/C)$ . These functions are expanded

$$D_1(q) = -\Lambda q - Bq^2 - \Gamma q^3 \\ D_n(q) = D_n + E_n q + F_n q^2 \quad (n = 2, 3, \dots), \quad (36)$$

and it is assumed that  $\Lambda$  and  $D_n$  are of zeroth order,  $B$  and  $E_n$  are of first order,  $\Gamma$  and  $F_n$  of second order, higher orders being neglected.<sup>5</sup> In principle, of course, Eq. 35 together with Eq. 36 determines both the equilibrium distributions and the fluctuation spectrum in terms of all the coefficients. Rather than solving Eq. 35 directly, Lax uses the set of equations for

<sup>4</sup>In fact, one finds by substituting  $P(q) = \delta(q - q_0)$  in Eq. 33 and computing  $(d/dt)\langle q \rangle$  from it, that  $G(q/C)$  is identical with  $\tilde{F}(q)$ .

<sup>5</sup>Apparently this refers to some “order of nonlinearity,” since it is not an expansion in a parameter. We shall show in Section 3.4 that a systematic expansion in a suitable parameter leads to the result that actually  $\Lambda$  and  $D_2$  are of zeroth order,  $B, E_2, D_3$  of first order,  $\Gamma, F_2, E_3, D_4$  of second order, etc. Moreover, a constant term should be included in  $D_1(q)$ , which is of second order and ensures that  $\langle q \rangle^{eq} = 0$ .

the successive *moments* of  $q$ ,

$$(d/dt)\langle q^k \rangle = -k(\Lambda\langle q^k \rangle + B\langle q^{k+1} \rangle + \Gamma\langle q^{k+2} \rangle) \\ + \sum_{n=2}^k \frac{k!}{(k-n)!} (D_n\langle q^{k-n} \rangle + E_n\langle q^{k-n+1} \rangle + F_n\langle q^{k-n+2} \rangle),$$

which follow immediately from Eq. 35. In order to find the fluctuation spectrum to second order one may omit all moments with  $k > 3$ . The resulting expression is too long to be reproduced here [Eqs. (14.48) with (14.49), (14.50), (14.59), (14.60) in Lax’s paper]. An essential remark is that the fluctuations spectrum is *not* uniquely determined by the phenomenological coefficients  $\Lambda, B, \Gamma$  alone, because it also involves the higher coefficients  $D_2, E_2, F_2, D_3, D_4$ .

Additional relations between these coefficients may be obtained, if one stipulates that  $P^{eq}$  must be Gaussian. However, to show that  $P^{eq}$  cannot be Gaussian, Lax mentions the following counterexample based on the work of J. Hopfield (unpublished). Consider an ideal rectifier [even more ideal than the one defined by Eq. 18!], with infinite impedance for  $V > 0$ , and zero impedance for  $V < 0$ . It is then argued that “the voltage fluctuations (and hence the charge fluctuations) on the condenser cannot be a Gaussian because voltage fluctuations above the threshold in the “easy” direction cannot occur.” This argument, however, is incorrect, because, although it may be possible to construct a rectifier whose *phenomenological* law approaches this ideal case, this phenomenological law cannot be valid in the realm of fluctuations. For such a device would be a Maxwell demon; if it is combined with an ordinary ohmic resistor to form a circuit, the voltage fluctuations produced in the resistor give rise to a nonzero average current. It will be shown in Section 3.3 that actually the Gaussian equilibrium distribution is valid under very general conditions.

#### 1.4 Formulation of the Problem

The work reported in the previous section led to the formulation of the following questions.

- i. Is it possible to describe the nonlinear case by means of a nonlinear F-P equation for  $P(q, t)$ , or does one have to add higher derivatives?
- ii. In the latter case, how does one measure the magnitude of the several terms?
- iii. Is the equilibrium distribution Gaussian, and is it true that the equilibrium average is shifted when the response is not symmetrical?

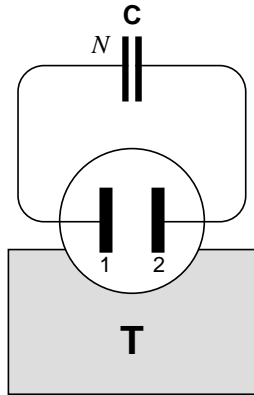


Figure 3: Alkemade's diode circuit.

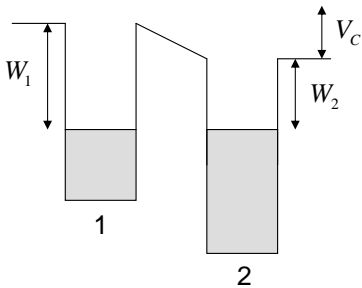


Figure 4: Graph of the potential in Alkemade's diode.

- iv. Is it possible to use  $P^{eq}(q)$  for obtaining relations between the coefficients of the equation for  $P(q, t)$ ?
- v. How is the phenomenological law related to the quantities occurring in the equation for  $P(q, t)$ ?
- vi. What is the fluctuation spectrum?

As the theory in Section 1.3 was unable to answer these questions, it is natural to turn to a model on which these questions can be investigated.

## 2 Diode Model

This section deals with a model that has led to the development of the theory in Section 3 and in fact contains all the essential features. Yet it is not indispensable for the understanding of the general theory in Section 3.

### 2.1 The Model

Alkemade (1958) introduced the model of a circuit and a vacuum diode valve consisting of two plane parallel electrodes of different metals (Fig. 3). The diode is idealized by assuming that the electrons in the diode vacuum space do not interfere with each other (no space charge) and that the transit time of the electrons is zero. The whole system is in equilibrium with a temperature bath. The work functions of both electrodes are supposed to be different, such that electrode 1 operates under saturation conditions, *i.e.*, it emits electrons at a constant rate independent of the potential difference (Fig. 4). Then the charge  $Q$  on the condenser obeys the same phenomenological law as the metal-oxide rectifier, Eq. 29.

The two terms in Eq. 29 are interpreted respectively as the probabilities per unit time for an electron to jump from electrode 1 to 2, and for a jump from 2 to 1. (This interpretation of the phenomenological law as determining directly the microscopic transition probabilities again amounts to identifying  $G$  with  $\tilde{G}$ .) By a kinetic calculation Alkemade then determines the high frequency limit

$$S_{\dot{q}}(\omega) \simeq \frac{2}{\pi} kTC\gamma_0 = \frac{2}{\pi} I_0 e. \quad (37)$$

[The value  $\gamma_0$  is taken from Eq. 30.] The same result was found by Lax (1960). It disagrees with the formula obtained by using the approach of MacDonald (1957), see Eq. 32,

$$S_{\dot{q}}(\omega) \simeq \frac{2}{\pi} kTC\gamma_0 \left( 1 - \frac{3}{4} \frac{e^2}{kTC} \right),$$

and with the result that is obtained with van Kampen's method,

$$S_{\dot{q}}(\omega) \simeq \frac{2}{\pi} kTC\gamma_0 \left( 1 + \frac{1}{6} \frac{e^2}{kTC} \right).$$

It will be shown in Section 3.2 that Eq. 37 is rigorously correct.

The theory of Alkemade's diode has been further developed by van Kampen (1960). Let  $N$  be the number of excess electrons on the condenser plate connected with electrode 1, so that the voltage difference is  $-eN/C$ . The probability per unit time for each of these electrons to jump to electrode 2 is some constant  $A$ . The probability for an electron on electrode 2 to leave it is  $A \exp[(W_1 - W_2)/kT]$ , but the probability that it leaves with sufficient kinetic energy to reach

electrode 1 is<sup>6</sup>

$$A \exp \left[ \left\{ \left( W_1 - \frac{e^2}{2C} (N+1)^2 \right) - \left( W_2 - \frac{e^2}{2C} N^2 \right) \right\} \frac{1}{kT} \right] \\ = A e^{\xi - \varepsilon N},$$

where

$$\xi = \frac{W_1 - W_2}{kT} - \frac{e^2}{2kTC}, \quad \varepsilon = \frac{e^2}{kTC}. \quad (38)$$

Consequently the probability distribution  $P_N(t)$  obeys the equation

$$\frac{1}{A} \frac{dP_N}{dt} = P_{N+1} - P_N + e^{\xi} \{ e^{-\varepsilon(N-1)} P_{N-1} - e^{-\varepsilon N} P_N \}. \quad (39)$$

This equation completely governs the behavior of the system under consideration and it is called the *master equation* (ME).

## 2.2 Conclusions from the model

First the equilibrium distribution can be found by solving Eq. 39 with  $dP_N/dt = 0$ . It is easily seen that the following solution holds:

$$P_N^{eq} = \text{const.} \exp \left[ -\frac{1}{2} \varepsilon N^2 + \frac{W_1 - W_2}{kT} N \right].$$

This is indeed Gaussian. The center is neither at  $\langle N \rangle^{eq} = 0$ , nor at  $\langle N \rangle^{eq} = -\frac{1}{2}$ , but at  $\langle N \rangle = N_C$ , where  $N_C$  corresponds to the contact potential:

$$eN_C/C = (W_1 - W_2)/e.$$

This answers question (iii). Marek (1959) has argued that the average voltage in equilibrium must vanish, because of the second law of thermodynamics. For his argument it is essential, however, that the two electrodes of the rectifier are made of the same metal, with another material in between, so that there are no contact potentials in the remaining circuit. Such a device is not described by our master equation (39).

Next we shall find the relation between the phenomenological law and the ME. One derives directly from 39, putting  $q = e(N - N_C)$ ,

$$\frac{d}{dt} \langle q \rangle = eA \left[ 1 - \left\langle e^{eq/kTC} \right\rangle e^{\varepsilon/2} \right]. \quad (40)$$

This differs from the phenomenological law (29) in two respects. First there is the factor  $e^{\varepsilon/2}$ . This factor is very near to 1 and unobservable in any actual experiment. Yet it is essential in a microscopic treatment

<sup>6</sup>This argument is due to Alkemade.

because it cancels the  $-\frac{1}{2} e$  in  $\langle q \rangle^{eq}$  [Eq. 31]. Note that the function  $\tilde{G}$ , defined in Eq. 22, is, according to Eq. 40, given by

$$(q/C)\tilde{G}(q) = eA \left[ 1 - e^{eq/kTC} e^{\varepsilon/2} \right], \quad (41)$$

so that it is incorrect to identify it with the phenomenological  $G$ . In fact, Eq. 41 could not serve as a response function for the diode, as it is not a function of  $V$  alone, but depends on  $C$  as well (through  $\varepsilon$ ).

The second difference is that the right-hand side of Eq. 40 contains  $\langle \exp[eq/kTC] \rangle$  instead of  $\exp[e\langle q \rangle/kTC]$ . The latter would be in accordance with MacDonald's general hypothesis, Eq. 15. The fact that the former appears has profound consequences. It is easily seen, on expanding in the same way as in Eq. 28, that the right-hand side does not depend on  $\langle q \rangle$  alone, but also on the higher moments  $\langle (q - \langle q \rangle)^2 \rangle$ , *etc.* Hence, Eq. 40 is not at all a differential equation from which  $\langle q \rangle$  can be solved as a function of time. In fact, one should not expect that the infinite set of differential equations (39) reduces to just a single equation for the average.

Nevertheless, it is possible to extract an equation for  $\langle q \rangle$  by a suitable limiting process. Indeed, let  $C \rightarrow \infty$ , keeping the voltage  $V = q/C$  fixed. Then  $e^{\varepsilon/2} \rightarrow 1$  and moreover, since the fluctuations in  $V$  are of order  $C^{-\frac{1}{2}}$  and hence tend to zero

$$\left\langle e^{eq/kTC} \right\rangle = \left\langle e^{eV/kT} \right\rangle \rightarrow e^{e\langle V \rangle/kT}.$$

Thus one obtains the phenomenological law from the equation for  $\langle q \rangle$  by going to the limit of infinite condenser, keeping the voltage fixed.

In order to compute the fluctuation spectrum from Eq. 39 it is necessary to expand.<sup>7</sup> The only available parameter is again  $\varepsilon$ , that is,  $1/C$ . However, as we are now dealing with the equilibrium state, the voltage  $V$  will now be itself of order  $C^{-\frac{1}{2}}$ , and  $q = -e(N - N_C)$  of order  $C^{\frac{1}{2}}$ . It is therefore convenient to introduce the normalized variable  $x$ ,

$$x = \varepsilon^{1/2}(N - N_C), \quad P_N(t) + \varepsilon^{1/2}P(x, t).$$

Then the Kramers-Moyal expansion of the ME (39) reads

$$\frac{1}{A} \frac{\partial P}{\partial t} = \varepsilon^{1/2} \frac{\partial P}{\partial x} + \frac{\varepsilon}{2} \frac{\partial^2 P}{\partial x^2} + \frac{\varepsilon^{3/2}}{3!} \frac{\partial^3 P}{\partial x^3} + \dots \quad (42) \\ + e^{-\varepsilon/2} \left\{ -\varepsilon^{1/2} \frac{\partial}{\partial x} + \frac{\varepsilon}{2} \frac{\partial^2}{\partial x^2} \right\} e^{-\varepsilon^{1/2}x} P.$$

<sup>7</sup>It happens that for the diode the fluctuation spectrum can be found exactly without expanding (van Kampen, 1961b), but that will not be true for most other cases.



The terms of order  $\varepsilon^{1/2}$  cancel, so  $\partial P/\partial t$  is of order  $\varepsilon$ , in agreement with the increase of relaxation time as  $C$  increases. It is therefore convenient to introduce the normalized time variable  $\tau = \varepsilon At$ . The equations for the moments are then found to be

$$\begin{aligned} (d/d\tau) \langle x \rangle &= -\langle x \rangle + \frac{\varepsilon^{1/2}}{2} (\langle x^2 \rangle - 1) \\ &\quad + \frac{\varepsilon}{2} \left( \langle x \rangle - \frac{1}{3} \langle x^3 \rangle \right) + O(\varepsilon^{3/2}) \\ (d/d\tau) \langle x^2 \rangle &= 2 - 2\langle x^2 \rangle + \varepsilon^{1/2} (\langle x^3 \rangle - 2\langle x \rangle) + O(\varepsilon) \\ (d/d\tau) \langle x^3 \rangle &= -3\langle x^3 \rangle + 6\langle x \rangle + O(\varepsilon^{1/2}). \end{aligned} \quad (43)$$

It is again true that the equation for  $\langle x \rangle$  involves all higher moments, but they occur with successively higher powers of  $\varepsilon$ . Consequently, it is possible to obtain a closed set of equations if one only wants to know  $\langle x \rangle$  to a certain order. Thus Eqs. 43 permit one to compute the conditional average  $\langle x \rangle_{x_0}$  to first order in  $\varepsilon$ . This leads to the autocorrelation function and hence to the fluctuation spectrum

$$\begin{aligned} S_{\dot{x}}(\omega) &= \quad (44) \\ \frac{2}{\pi} \left[ (1 - \varepsilon) \frac{\omega^2}{(1 - \frac{1}{2}\varepsilon)^2 + \omega^2} + \frac{\varepsilon}{4} \frac{\omega^2}{1 + (\omega/2)^2} \right] + O(\varepsilon^2). \end{aligned}$$

This answers question (vi). Compare the result with Eq. 32, noting that in the present units  $kTC = \tilde{\gamma}_0 = 1$ . The high-frequency limit agrees with Eq. 37, as it should.

Clearly, question(iv) cannot be settled by studying a special model for which all coefficients in the equation for  $P$  are known; it will be further discussed in Section 3.6.

### 2.3 Validity of the Fokker-Planck Equation

In order to assess the validity of the F-P equation, we write the expansion of Eq. 42 explicitly

$$\begin{aligned} \frac{\partial P}{\partial \tau} &= \frac{\partial}{\partial x} \left\{ x - \frac{\varepsilon^{1/2}}{2} (x^2 - 1) + \frac{\varepsilon}{6} (x^3 - 3x) \right\} P \\ &\quad + \frac{\partial^2}{\partial x^2} \left\{ 1 - \frac{\varepsilon^{1/2}}{2} x + \frac{\varepsilon}{4} (x^2 - 1) \right\} P \\ &\quad + \frac{\partial^3}{\partial x^3} \left\{ \frac{\varepsilon}{6} x \right\} P + \frac{\varepsilon}{12} \frac{\partial^4 P}{\partial x^4}. \end{aligned} \quad (45)$$

The zero-order term constitutes the linear F-P equation (14). To order  $\varepsilon^{1/2}$  the equation is a nonlinear F-P equation: the linear coefficient has been supplemented with a quadratic term, and the constant coefficient of the second derivative has become a linear function. Note that in the former also a constant

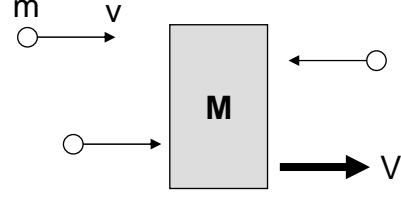


Figure 5: **The Rayleigh particle.**

term  $\frac{1}{2} \varepsilon^{1/2}$  has appeared, which was not present in the phenomenological law (29) and which cancels the anomalous result of Eq. 31. To this order  $\varepsilon^{1/2}$ , however, there are no corrections yet to the fluctuation spectrum.

The first order in  $\varepsilon$  adds higher corrections to the same coefficients, but at the same time it brings in higher derivatives. This shows that *it is inconsistent to use the F-P equation for the nonlinear case*, as was done by MacDonald, van Kampen and Davies. It is also inconsistent to write all higher derivatives, while including the nonlinearity only to a certain order, as was done by Lax. There is just one single parameter  $\varepsilon$ , which determines both the amount of nonlinearity and the validity of the Fokker-Planck equation. This answers questions (i) and (ii).

The mathematical proof of the Fokker-Planck equation (Khintchine, 1933; Middleton, 1960) suggests its validity for practically all Markov processes, apart from some rather unrestrictive additional assumptions. Actually these assumptions are crucial: they amount to postulating that the individual transitions are infinitely small. In the case of the diode this can only be achieved by taking  $C$  large, which at the same time has the effect of destroying the influence of the nonlinearity on the fluctuations.

A similar situation prevails in the case of a Rayleigh particle. Rayleigh (1891; Zernike, 1929) studied the probability distribution  $P(V, t)$  of one velocity component  $V$  of a heavy particle, mass  $M$ , immersed in a gas of molecules of mass  $m$  (Fig. 5). It is convenient to picture the particle as a flat disc or piston. The individual transitions are due to collisions of the gas molecules and are of order

$$\Delta V \sim m\bar{v}/M \sim (m/M)(kT/m)^{1/2}.$$

In equilibrium,  $V$  is of order  $\bar{V} \sim (kT/M)^{1/2}$ , so that the F-P equation is a valid approximation if

$$1 \gg \Delta V/V \sim (m/M)^{1/2}. \quad (46)$$

On the other hand, the damping law will be linear as long as  $V \ll \bar{v}$ ; hence the equilibrium fluctuations are not influenced by the nonlinearity if  $\bar{V} \ll \bar{v}$ , or  $M^{-1/2} \ll m^{-1/2}$ . Again this is the same condition as Eq. 46. The purpose of the next chapter is to show that this state of affairs is general, but two qualifying remarks must be made.

First, for the purpose of finding the phenomenological law, the nonlinear F-P equation may be used, provided that the fluctuations are neglected. Indeed, the nonlinear F-P equation is obtained by erasing the third and higher derivatives in the Kramers-Moyal expansion (42). Obviously these terms do not contribute to  $(d/dt)\langle x \rangle$ . Hence the nonlinear F-P equation leads to the exact result (40), which reduces to the phenomenological law in the limit in which the fluctuations are neglected. This remark justifies the use of the nonlinear F-P equation for deriving nonlinear generalizations of Onsager's reciprocal relations (van Kampen, 1957; Uhlhorn, 1960).

Secondly, for the purpose of computing the fluctuation spectrum the nonlinear F-P equation is slightly better than would appear from the above criticism. The spectrum to order  $\varepsilon$  only requires  $\langle x \rangle$  to order  $\varepsilon$ , and therefore  $\langle x^2 \rangle$  to order  $\varepsilon^{1/2}$  and  $\langle x^3 \rangle$  to order  $\varepsilon^0$ . The third and higher derivatives in Eq. 42 do not affect the first two moments, and contribute to  $\langle x^3 \rangle$  only in order  $\varepsilon^{1/2}$ . Thus the nonlinear F-P equation still gives the correct fluctuation spectrum to order  $\varepsilon$ ; but for the terms of order  $\varepsilon^2$ , the higher derivatives are indispensable.

### 3 General Theory

#### 3.1 Statistical Foundations

We are concerned with systems that consist of a very large number  $\mathcal{N}$  of particles. In classical theory, the precise *microscopic* state of the system is described by  $6\mathcal{N}$  variables  $x_1, \dots, x_{3\mathcal{N}}, p_1, \dots, p_{3\mathcal{N}}$ . They obey the  $6\mathcal{N}$  microscopic equations of motion. The gross, *macroscopic* aspect of the state is described by a much smaller number of variables  $Q_1, \dots, Q_n$ , which are functions of  $x_1, \dots, p_{3\mathcal{N}}$ . For convenience we suppose that apart from the energy there is just one other  $Q$ , and drop the label. Experience tells us the remarkable fact that this macroscopic variable  $Q(x_1, \dots, p_{3\mathcal{N}})$  obeys again a differential equation

$$\dot{Q} = F(Q), \quad (47)$$

which permits to uniquely determine its future values from its value at some initial instant. The phenomenological law (47) is *not* a purely mathematical

consequence of the microscopic equations of motion. The reason why it exists can be roughly understood as follows. Using the equations of motion one has

$$\dot{Q} = \sum_{k=1}^{3\mathcal{N}} \left( \frac{\partial Q}{\partial x_k} \dot{x}_k + \frac{\partial Q}{\partial p_k} \dot{p}_k \right) \equiv g(x_1, \dots, p_{3\mathcal{N}}).$$

The variables in  $g$  may be expressed in  $Q$  and the energy (which we do not write explicitly), and  $6\mathcal{N} - 2$  remaining variables,  $\vartheta_\lambda(x_1, \dots, p_{3\mathcal{N}})$  say. Hence

$$\dot{Q} = f(Q; \vartheta_1, \dots, \vartheta_{6\mathcal{N}-2}).$$

This may also be written

$$Q(t + \Delta t) - Q(t) = \int_t^{t+\Delta t} f[Q(t'); \vartheta(t')] dt'.$$

Now suppose that  $Q(t)$  varies much more slowly than the  $\vartheta_\lambda$  (which is the reason it is microscopic). It is then possible to pick  $\Delta t$  such that  $Q(t)$  does not vary much during  $\Delta t$ , while the  $\vartheta_\lambda$  practically run through all their possible values (ergodic theorem with fixed value for  $Q$ ). Hence one may substitute in the integral  $Q(t)$  for  $Q(t')$  and replace the time integration by an average over that part of the phase space that corresponds to given values of the energy and  $Q$ :

$$Q(t + \Delta t) - Q(t) = \Delta t \cdot \langle f[Q(t); \vartheta] \rangle_{Q(t)} = \Delta t \cdot F[Q(t)].$$

It should be emphasized that this implies that at each time  $t$  the  $\vartheta_\lambda$  vary in a sufficiently random way to justify the use of a phase space average ("repeated randomness assumption").

Fluctuations arise from the fact that, in the relevant part of phase space,  $f$  is not exactly equal to its average  $F$ , but has a probability distribution around it. Hence  $Q(t + \Delta t)$  is no longer uniquely determined by  $Q(t)$ , but instead there exists a transition probability  $W(q'|q)$ . More precisely,  $\Delta t W(q'|q) dq'$  is the probability that, if  $Q$  has the value  $q$  at time  $t$ , the value of  $Q(t + \Delta t)$  will lie between  $q'$  and  $q' + dq'$ . The probability distribution  $P(q, t)$  of  $Q$  at any time  $t$  then obeys the rate equation

$$\frac{\partial P(q, t)}{\partial t} = \int \{W(q|q')P(q', t) - W(q'|q)P(q, t)\} dq'. \quad (48)$$

This is the general form of the master equation, of which Eq. 39 is a special case. It can also be derived in quantum mechanics by an essentially similar argument (van Kampen, 1954, 1956, 1962; van Hove, 1955, 1962; Prigogine, 1962). Again a repeated randomness

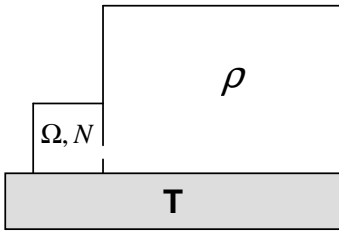


Figure 6: **Density fluctuations in the volume  $\Omega$ .**

assumption is involved, namely that at each time the  $\vartheta_\lambda$  are sufficiently random to justify the identification of probability with measure in phase space.

A formally equivalent way of writing the ME is obtained by expanding in powers of  $q' - q$ ,

$$\frac{\partial P(q, t)}{\partial t} = \sum_{n=1}^{\infty} \frac{1}{n!} \left( -\frac{\partial}{\partial q} \right)^n \alpha_n(q) P(q, t), \quad (49)$$

where  $\alpha_n(q)$  are the successive moments of the transition probability, or “derivate moments,”

$$\alpha_n(q) = \int (q' - q)^n W(q'|q) dq'.$$

They are identical with the  $D_n(q)$  in Eq. 35 apart from a factor  $n!$ .

*EXAMPLE 1. Alkemade’s diode* (cf. Section 2.1 and Figs. 3 and 4). The macroscopic variable  $Q$  is the charge on the condenser, or the number  $N$  of excess electrons on one condenser plate. The remaining variables  $\vartheta_\lambda$  are all other quantities needed to specify the microscopic state of the electrons and the heat bath. The transition probability is, according to Eq. 39,

$$W(N'|N) = A\delta_{N',N-1} + Ae^{\xi - \varepsilon N} \delta_{N',N+1}. \quad (50)$$

*EXAMPLE 2. Density fluctuations.* A box of volume  $\Omega$  communicates through a small hole with a very large volume, filled with a dilute gas with density  $\rho$  (Fig 6). For  $Q$  we take the number  $N$  of molecules in  $\Omega$ , while the remaining set of variables  $\vartheta$  consists of all momenta of the molecules and practically all of their coordinates, restricted only by the condition that exactly  $N$  of them must be in  $\Omega$ . It is easily seen that the procedure described above leads to the ME (with suitably chosen time unit)

$$\begin{aligned} \frac{\partial P(N)}{\partial t} &= \frac{N+1}{\Omega} P(N+1) - \frac{N}{\Omega} P(N) \\ &+ \rho \{P(N-1) - P(N)\}. \end{aligned} \quad (51)$$

*EXAMPLE 3. Rayleigh’s piston* (cf. Section 2.3 and Fig. 5). There are two macroscopic variables, namely the coordinate and the velocity of the heavy particle; the coordinates and momenta of the gas particles are the variables  $\vartheta_\lambda$ . Of the two phenomenological equations, the one connecting the coordinate with the velocity is trivial. The other one is the phenomenological damping law for the velocity and does not involve the coordinates. In order to describe the fluctuations it is replaced by a ME, the transition probability being

$$\begin{aligned} W(V'|V) &= nA \left( \frac{M+m}{2m} \right)^2 |V' - V| \times \\ &f \left( \frac{M+m}{2m} V' - \frac{M-m}{2m} V \right). \end{aligned} \quad (52)$$

Here  $n$  is the number of molecules per  $cm^3$ ,  $f$  is their velocity distribution,  $A$  the surface area of the piston.

*EXAMPLE 4. Brownian particle.* The same particle studied on a longer time scale, so that the instantaneous velocity is not observed. The macroscopic variable is the coordinate, while the  $\vartheta_\lambda$  now also include the velocity of the heavy particle. The right-hand side of Eq. 47 is now zero, the displacement of the particle is wholly due to fluctuations. Kramers (1940) has given a general treatment, which comprises both the Rayleigh and Brownian aspect.

*EXAMPLE 5. n-type semiconductor.* The macroscopic variable is the number  $N$  of electrons in the conduction band, the  $\vartheta_\lambda$  are all other variables. The transition probability has the form (Burgess, 1955a,b, 1956; van der Ziel, 1959)

$$W(N'|N) = r(N)\delta_{N',N-1} + g(N)\delta_{N',N+1}, \quad (53)$$

where  $r(N)$  and  $g(N)$  are linear or quadratic functions of  $N$ , depending on the kind of semiconductor considered. In particular, for the strongly extrinsic semiconductor

$$r(N) = r_0\omega \left( \frac{N}{\Omega} \right)^2, \quad g(N) = g_0\omega \left( n_d - \frac{N}{\Omega} \right) \quad (54)$$

where  $r_0$  and  $g_0$  are constants,  $\Omega$  the volume,  $n_d$  the number of donors per unit volume.

### 3.2 General Properties of the Master Equation

The master equation (48) is of the form

$$\dot{P} = \mathbf{W}P, \quad (55)$$

where  $\mathbf{W}$  is a linear operator acting on functions of  $q$ . Equations of this form occur in many parts of physics: diffusion, heat conduction, Schrödinger equation, Liouville equation, *etc.* For the familiar mathematical techniques of eigenvalues and eigenfunctions, however, it is essential that  $\mathbf{W}$  be a symmetrical or self-adjoint operator. Fortunately, the transition probabilities have the property of reciprocity, which is almost as good.

To formulate reciprocity, one must distinguish between even and odd macroscopic variables.  $Q$  is said to be *even* when it is an even function of all velocities, so that its value remains the same if the microscopic motion of all particles is reversed. It is an *odd* variable when it changes sign on reversing motion. In the third example above,  $V$  is an odd variable, in the other examples the macroscopic variables are even.

Both when  $Q$  is even and when  $Q$  is odd one has  $P^{eq}(q) = P^{eq}(-q)$ . When  $Q$  is even, reciprocity states

$$W(q'|q)P^{eq}(q) = W(q|q')P^{eq}(q'), \quad (56)$$

which is also called “microscopic reversibility” or “detailed balance,” and can be proved generally (Wigner, 1954; van Kampen, 1954). It is convenient to define a “scalar product” of any two functions  $P_1(q)$  and  $P_2(q)$  by

$$(P_1, P_2) = \int P_1(q)P_2(q) \frac{dq}{P^{eq}(q)}, \quad (57)$$

so that Eq. 56 can be expressed by

$$(P_1, \mathbf{W}P_2) = (P_2, \mathbf{W}P_1) = (\mathbf{W}P_1, P_2), \quad (58)$$

which states that  $\mathbf{W}$  is self-adjoint. In addition, one may deduce from Eq. 56 and the fact that  $W(q|q') \geq 0$ ,

$$(P, \mathbf{W}P) \leq 0. \quad (59)$$

More generally, let  $f(x)$  be a concave function [*i.e.*,  $f''(x) \geq 0$ ]; then it can be shown in the same way that

$$H = \int P^{eq} f(P/P^{eq}) dq$$

never increases. Particular choices are

$$\begin{aligned} H &= \int P \log(P/P^{eq}) dq \quad \text{and} \\ H &= \int (P^2/P^{eq}) dq; \end{aligned} \quad (60)$$

the former is minus the Gibbs entropy and the latter will be used in Section 3.5.

By setting  $P(q, t) = e^{\lambda t} P_\lambda(q)$ , Eq. 55 is reduced to the eigenvalue problem

$$\mathbf{W}P_\lambda = -\lambda P_\lambda. \quad (61)$$

The eigenfunctions  $P_\lambda$  are mutually orthogonal in terms of the scalar product (57). Because of Eq. 59 one has  $\lambda \geq 0$ . There is an eigenvalue  $\lambda = 0$  with eigenfunction  $P_0(q) \equiv P^{eq}(q)$ . It may be assumed that this eigenvalue is not degenerate because it can be shown that otherwise  $\mathbf{W}$  is reducible, so that the ME decomposes into a number of separate master equations. For convenience, we also assume that the eigenvalues are discrete; in some cases (diffusion, Brownian movement), the spectrum is continuous, which requires only minor modifications.

If one has a complete set of eigenfunctions  $P_\lambda$ , normalized to  $(P_\lambda, P_\lambda) = 1$ , the completeness relation

$$\sum_\lambda P_\lambda(q)P_\lambda(q') = P^{eq}(q) \cdot \delta(q - q')$$

holds. Consequently, the solution of the ME that reduces to  $\delta(q - q_0)$  for  $t = 0$  is

$$P_t(q|q_0) = \sum_\lambda e^{-\lambda t} P_\lambda(q)P_\lambda(q_0)/P^{eq}(q_0). \quad (62)$$

This is the transition probability from  $q_0$  to  $q$  in time  $t$ . Hence the autocorrelation function is

$$\begin{aligned} \langle q_0 \langle q(t) \rangle_{q_0} \rangle^{eq} &= \int P^{eq}(q_0)q_0 dq_0 \int P_t(q_0|q)q dq \\ &= \sum_\lambda e^{-\lambda t} \left[ \int P_\lambda(q)q dq \right]^2. \end{aligned} \quad (63)$$

The fluctuation spectrum of  $q$  is therefore

$$S_q(\omega) = \frac{2}{\pi} \sum_\lambda \frac{\lambda}{\lambda^2 + \omega^2} \left[ \int P_\lambda(q)q dq \right]^2. \quad (64)$$

An asymptotic expression for high frequencies is obtained by expanding each term in  $1/\omega^2$ :

$$S_q(\omega) \simeq \frac{2}{\pi} \sum_{n=0}^{\infty} \left( -\frac{1}{\omega^2} \right)^{n+1} \langle q \tilde{\mathbf{W}}^{2n+1} q \rangle^{eq},$$

where  $\tilde{\mathbf{W}}$  is the transposed operator of  $\mathbf{W}$ , defined by

$$\int f(q) \mathbf{W}g(q) dq = \int g(q) \tilde{\mathbf{W}}f(q) dq,$$

for any  $f$  and  $g$ . In particular, one has

$$\lim_{\omega \rightarrow \infty} S_q(\omega) = -\frac{2}{\pi} \langle q \tilde{\mathbf{W}} q \rangle^{eq}.$$

Inserting  $\mathbf{W}$  from Eq. 50, one obtains Alkemade's result (37).

When  $Q$  is an odd variable, reciprocity consists of two equations

$$W(q'|q)P^{eq}(q) = W(-q|-q')P^{eq}(q'),$$

$$\int W(q'|q) dq' = \int W(-q'|-q) dq'.$$

Whether the previous work can be extended to this case has not been fully investigated. However, in some simple cases, like the Rayleigh particle,  $\mathbf{W}$  also obeys Eqs. 58 and 59, even though the variable is odd, so that the previous work applies.

### 3.3 The Equilibrium Distribution

When deriving Eq. 56, the function  $P^{eq}(q)$  enters as a volume of phase space; it is then found *a posteriori* from Eq. 56 that  $P^{eq}(q)$  is indeed a time-independent solution of the ME (48). The explicit form of  $P^{eq}(q)$  is a matter of equilibrium statistical mechanics. In the linear theory,  $P^{eq}(q)$  is always taken to be a Gaussian. As mentioned in Section 1.3, MacDonald (1957) raised the question whether this is still correct in the presence of nonlinearity. Indeed, that this cannot always be correct is obvious from the example of the density fluctuations, for the equilibrium distribution must be a Poisson function, as is easily verified from Eq. 51. On the other hand, the examples of the diode and the Rayleigh particle demonstrate that a nonlinear phenomenological law is not necessarily incompatible with a Gaussian equilibrium distribution. The following theorem seems to cover most cases.

The equilibrium distribution is a Gaussian function of the microscopic variable  $q$  if

- i. the energy of the total system is quadratic in  $q$ ; and
- ii. the interaction (*i.e.*, that part of the total Hamiltonian of the system that is responsible for transitions between different values of  $q$ ) has a strength parameter which enters  $W(q|q')$  as a factor that permits one to scale down the magnitude of  $W(q|q')$  without affecting its functional dependence on  $q$  and  $q'$ .

Condition (i) ensures that, according to equilibrium statistical mechanics

$$P^{eq}(q) \propto \exp(-cq^2). \quad (65)$$

This condition rules out the case of the density fluctuations. The second condition is necessary as Eq. 65

is only exact for infinitely small interaction. The strength parameter permits one to go to this limit, without altering the form of  $P^{eq}$ . Hence, Eq. 65 must be exact for all values of the strength parameter because  $P^{eq}(q)$  does not depend on the magnitude of  $W(q|q')$ , but only on its functional dependence on  $q$  and  $q'$ .

Both conditions are fulfilled for the diode model, the strength parameter being the surface area of the electrodes; and for the Rayleigh piston, the strength parameter being the area  $A$  of the piston.

### 3.4 Power Series Expansion of the Master Equation

The ME can be solved exactly for the example of density fluctuations, Eq. 51, and for the example of the diode, Eq. 39 (van Kampen, 1961b). In most other cases an approximation method has to be used. In order to avoid the ambiguities reported in Section 1.3, *it is essential to use a systematic expansion*, like in Section 2.2. To find a suitable expansion parameter, analogous to  $\varepsilon = e^2/kTC$  in Section 2.2, we note: (i) the magnitude of the fluctuations is usually given in terms of an *extensive* quantity, like charge or number of particles; (ii) the dependence of the transition probability is properly expressed through an *intensive* quantity, like voltage or particle density. Supposing  $q$  to denote an extensive quantity, we introduce the corresponding intensive quantity  $X = q/\Omega$ , where  $\Omega$  is some measure for the size of the system. It is then natural to write for the transition probability

$$W(q'|q) = \Phi\left(\frac{q}{\Omega}; q' - q\right) = \Phi(X; q' - q). \quad (66)$$

We expect that  $\Phi$ , in contrast to  $W$ , no longer depends implicitly on  $\Omega$ . This is indeed for density fluctuations, Eq. 51; and for the Rayleigh particle, Eq. 52, on putting

$$X = V, \quad q = \frac{M+m}{m} V, \quad \Omega = \frac{M+m}{m}. \quad (67)$$

It is also true for the strongly extrinsic semiconductor described by Eqs. 53 and 54, except for a factor  $\Omega$  in  $\Phi$ , which can easily be removed by a change in time scale. It is clear from Eq. 66 that  $\Omega$  measures the relative magnitude of the fluctuations: as  $\Omega \rightarrow \infty$ , the fluctuations in  $X$  tend to zero, so that they can be made small compared to the range over which the phenomenological function  $G(X)$  varies materially. Therefore, we shall expand in reciprocal powers of  $\Omega$ .

For this purpose we make all powers of  $\Omega$  explicit by

the following transformation of variables,

$$t = \Omega\tau \quad (68)$$

$$q = \Omega\varphi(\tau) + \Omega^{1/2}x, \quad q' = q + \Delta q, \quad (69)$$

$$P(q, t) = P(\Omega\varphi(\tau) + \Omega^{1/2}x, \Omega\tau) \equiv \Pi(x, \tau). \quad (70)$$

Equation (68) takes account of the increasing relaxation time.<sup>8</sup> Equation (69) expresses that  $q$  consists of two parts: the macroscopic part  $\Omega\varphi(\tau)$ , whose dependence on time is described by  $\varphi(\tau)$  and will be determined presently; and a fluctuating part, which will be of order  $\Omega^{1/2}$ . When this is substituted in Eq. 49, the expansion in  $\Omega$  is straightforward. We write  $\alpha_n^{(p)}(X)$  for the  $p^{\text{th}}$  derivative with respect to  $X$  of the derivate moment  $\alpha_n$ . One finds after some manipulations (van Kampen, 1961a)

$$\begin{aligned} \frac{\partial \Pi}{\partial \tau} - \Omega^{1/2}\varphi'(\tau)\frac{\partial \Pi}{\partial x} &= -\Omega^{1/2}\alpha_1\{\varphi(\tau)\}\frac{\partial \Pi}{\partial x} \quad (71) \\ + \sum_{m=2}^{\infty} \frac{\Omega^{-\frac{1}{2}(m-2)}}{m!} \sum_{n=1}^m \binom{m}{n} \alpha_n^{(m-n)}\{\varphi(\tau)\} &\left(\frac{-\partial}{\partial x}\right)^n x^{m-n}\Pi. \end{aligned}$$

First, equating the terms of order  $\Omega^{1/2}$ , one finds the phenomenological law

$$\frac{d\varphi}{d\tau} = \alpha_1(\varphi), \quad \text{or} \quad \frac{dq}{dt} = \alpha_1(X). \quad (72)$$

This determines  $\varphi(\tau)$  for any given initial value  $\varphi(0)$ . Inserting this result in (71), one obtains an equation for the probability distribution  $\Pi(x, \tau)$  of the fluctuations around the macroscopic value. The two lowest orders are

$$\begin{aligned} \frac{\partial \Pi}{\partial \tau} &= -\frac{\partial}{\partial x} \left[ \alpha_1^{(1)}x + \frac{1}{2}\Omega^{-1/2}\alpha_1^{(2)}x^2 + \dots \right] \Pi \\ &+ \frac{1}{2}\frac{\partial^2}{\partial x^2} \left[ \alpha_2^{(0)} + \Omega^{-1/2}\alpha_2^{(1)}x + \dots \right] \Pi \\ &- \frac{1}{3!}\frac{\partial^3}{\partial x^3} \left[ \Omega^{-1/2}\alpha_3^{(0)} + \dots \right] \Pi. \quad (73) \end{aligned}$$

All  $\alpha_n^{(p)}$  are to be taken at  $\varphi(\tau)$ , or, if one is interested in equilibrium fluctuations, at  $\varphi(\infty)$ . The two zero order terms constitute the linear Fokker-Planck equation (14). The next order corrects the coefficients of both terms, and adds a third derivative. Similarly, each higher order of  $\Omega^{-1/2}$  adds one higher derivative. Hence the result found in Section 2.2 for the diode is general: It is inconsistent to use the F-P equation

<sup>8</sup>This transformation is not required when the fluctuations are a bulk property, as for chemical reactions or for carrier fluctuations in semiconductors [cf. Eq. 54]

for the nonlinear case, but it is equally inconsistent to add higher derivatives without at the same time correcting the coefficients of the lower derivatives.

*Additional remark.* In the case of the Rayleigh particle it is customary to expand in  $m/M$  rather than in  $m/(M+m)$ . This amounts to putting, instead of Eq. 67,

$$X = V, \quad q = MV/m, \quad \Omega = M/m.$$

In that case,  $\Phi$  is not independent of  $\Omega$ , see Eqs. 52 and 66. In more elaborate examples, this is even unavoidable, for instance if the Rayleigh particle is immersed in a mixture of gases (Alkemade *et al.*, 1963). However, that does not invalidate the above expansion method because it is still true that  $\Phi$  is a power series in  $1/\Omega$ . The only consequence is that the  $\alpha_n$  are also power series in  $1/\Omega$ ,

$$\alpha_n(X) = \alpha_{n,0}(X) + \Omega^{-1}\alpha_{n,1}(X) + \dots \quad (74)$$

It is then consistent to identify the phenomenological law not with Eq. 72, but with its lowest order,

$$dq/dt = \alpha_{1,0}(X).$$

The terms with  $\alpha_{1,1}(X)$ , *etc.*, are to be included in the equation (73) for  $\Pi$ .<sup>9</sup> Moreover, the  $\alpha_n^{(p)}$  in (73) involve higher powers of  $1/\Omega$ , which should only be included as far as necessary.

### 3.5 Siegel's Expansion

The ME (55) has the essential property that  $\mathbf{W}$  is "negative semi-definite" in the sense that it has one eigenvalue  $\lambda = 0$  with eigenfunction  $P^{eq}$ , all other eigenvalues being negative. This property guarantees that every solution tends to  $P^{eq}$  for  $t \rightarrow \infty$ . The successive approximations in the expansion of Section 3.4, however, do not all have this property. Siegel (1960) has shown that this can be remedied by the following procedure.

As  $-\mathbf{W}$  is positive semidefinite, it has a square root  $\mathbf{U}$ , in the sense that

$$-\mathbf{W} = \mathbf{U}\mathbf{U} = \mathbf{U}^2,$$

where  $\mathbf{U}$  is another self-adjoint operator.<sup>10</sup> In fact one readily verifies

$$U(q|q') = \sum_q \sqrt{\lambda} P_\lambda(q) P_\lambda(q') / P^{eq}(q'). \quad (75)$$

<sup>9</sup>This also occurs in the diode; for instance the terms  $\frac{1}{2}\varepsilon^{1/2}$  and  $-\frac{1}{2}\varepsilon x$  on the first line of Eq. 45 are of this nature.

<sup>10</sup>Actually Siegel writes  $\mathbf{W} = -\mathbf{U}\mathbf{U}^\dagger$ , so that  $\mathbf{U}$  need not be self-adjoint.

Now suppose  $\mathbf{W}$  has been expanded in  $\Omega^{-1/2}$ , to second order, say. One may then also write for  $\mathbf{U}$  a quadratic expression in  $\Omega^{-1/2}$  and determine the coefficients  $\mathbf{U}_0, \mathbf{U}_1, \mathbf{U}_2$ , successively, from the requirement

$$-(\mathbf{U}_0 + \Omega^{-1/2}\mathbf{U}_1 + \Omega^{-1}\mathbf{U}_2)^2 = \mathbf{W} + O(\Omega^{-3/2}).$$

the left-hand side is then a correct approximation to second order, and self-adjoint and negative semidefinite by construction, thanks to the addition of some terms of higher order.

In the second part of his paper, Siegel gives the following expansion for the operator  $\mathbf{W}$ .<sup>11</sup> It is assumed that  $P^{eq}(q)$  is Gaussian and is given by Eq. 65 with  $c = \frac{1}{2}$ . We start from the ME in the form (49) and expand the  $\alpha_n(q)$  in Hermite polynomials

$$\alpha_n(q) = \sum_{k=0}^{\infty} \alpha_{nk} H_k(q), \quad H_k(q) = e^{\frac{1}{2}q^2} \left(-\frac{d}{dq}\right)^n e^{-\frac{1}{2}q^2}.$$

One then has

$$\frac{\partial P}{\partial t} = e^{-\frac{1}{2}q^2} \sum_{n,k} \frac{\alpha_{nk}}{n!} \left(\frac{q}{2} - \frac{\partial}{\partial q}\right)^n H_k(q) e^{\frac{1}{2}q^2} P.$$

We substitute the mathematical identity

$$H_k(q) = \sum_{l=0}^k \binom{k}{l} \left(\frac{q}{2} - \frac{d}{dq}\right)^{k-l} \left(\frac{q}{2} + \frac{d}{dq}\right)^l,$$

and obtain after some rearrangements Siegel's expansion

$$\frac{\partial P}{\partial t} = e^{-\frac{1}{2}q^2} \sum_{m=0}^{\infty} \sum_{l=0}^m A_{lm} \left(\frac{q}{2} - \frac{\partial}{\partial q}\right)^{k-l} \left(\frac{q}{2} + \frac{\partial}{\partial q}\right)^l e^{\frac{1}{2}q^2} P, \quad (76)$$

where

$$A_{lm} = \frac{1}{\sqrt{2\pi}} \frac{1}{l!} \sum_{k=l}^m \frac{\int_{-\infty}^{\infty} \alpha_{m-k+1}(q) H_k(q) e^{-\frac{1}{2}q^2} dq}{(k-l)!(m-k+1)!}.$$

From the fact that  $e^{-q^2/2}$  must obey Eq. 76, it follows that all  $A_{0m}$  must vanish. The first non-vanishing term, with  $m = 1, l = 1$ , is just the linear F-P equation. For self-adjointness, one must have  $A_{l,m} = A_{m-l+1,m}$ , which implies a property of the  $\alpha_{n,k}$ , but this has not been investigated.

<sup>11</sup>The present derivation is somewhat different from the original one.

Equation (76) is not a power series expansion in a parameter. Siegel suggests that the magnitude of the successive terms with  $m = 1, 2, \dots$  should be estimated from their contributions to  $dH/dt$ , where  $H$  is taken from the second expression in Eq. 60. In the spirit of Section 3.4, however, it can also be verified that  $A_{lm}$  is of order  $\Omega^{-m/2}$ , although it includes higher orders, too. In addition, when breaking off at a certain  $m$ , the operator must still be made negative semidefinite by applying the above-mentioned procedure.

After constructing in this way an approximate  $\mathbf{W}$ , which is self-adjoint, negative semidefinite, and correct to some order  $\Omega^{-m/2}$ , one may compute from it the fluctuation spectrum to that same order, for instance, by means of Eq. 64. The result is identical with the one obtained in a less laborious way by mean of the expansion (73). However, in the latter case Eq. 64 is unsuitable because some of the eigenvalues  $\lambda$  may turn out positive or complex, since Eq. 73 is not self-adjoint and negative definite in each order. Instead, one must treat the higher order terms in Eq. 73 as perturbations of the linear F-P equation.<sup>12</sup>

### 3.6 The Connection between Fluctuations and Dissipation

In the linear theory of Section 1.2, the fluctuation spectrum of  $q$  was calculated from Eqs. 4 and 5, without using Eq. 6. The fluctuation spectrum of  $\kappa$  is then also known:

$$\begin{aligned} S_{\kappa}(\omega) &= (\gamma_0^2 + \omega^2) S_q(\omega) \\ &= (2/\pi) \gamma_0 \langle q^2 \rangle^{eq} = (2/\pi) kTC \gamma_0. \end{aligned}$$

This agrees with the autocorrelation function (6), provided that

$$\Gamma = 2kTC \gamma_0 = 2kT/R. \quad (77)$$

This is called the Nyquist relation (Nyquist, 1928), and is closely related to Einstein's relation for Brownian movement (Einstein, 1905, 1906). It connects a stochastic property of the electromotive force produced in the resistor with its dissipative property. The same relation is found in the Fokker-Planck approach by adjusting  $\Gamma$  in Eq. 14, so as to obtain the correct equilibrium distribution.

<sup>12</sup>An analogous situation prevails in the quantum mechanical calculation of the Stark effect. The exact Hamiltonian of an atom in an electric field has no discrete eigenvalues. Yet perturbation theory gives the correct shifts of the discrete eigenvalues of the unperturbed Hamiltonian.

One has to know  $\Gamma$  for calculating  $\langle q^2(t) \rangle$  from a given initial  $\langle q(0) \rangle$ . In fact, Eq. 77 is usually derived by doing just this and then using the fact that  $q^2(t)$  should tend to  $\langle q^2 \rangle^{eq} = kTC$  as  $t \rightarrow \infty$  (Uhlenbeck and Ornstein, 1930). Thus the Nyquist theorem implies that, for linear systems, the mean square of the fluctuations can be found as a function of time from the macroscopic damping constant alone, without knowing anything about the detailed mechanism that causes the fluctuations. The higher moments, like  $\langle q^4(t) \rangle$ , however, involve higher moments of  $\kappa(t)$ , like

$$\langle \kappa(t)\kappa(t')\kappa(t'')\kappa(t''') \rangle,$$

and cannot therefore be found without knowing more about this fluctuating force.<sup>13</sup>

The question of how to extend the Nyquist relation to nonlinear systems may be formulated as follows. The equilibrium fluctuations are described by Eq. 73, the coefficients  $\alpha_n^{(p)}$  all being taken at the equilibrium value  $\varphi(\infty)$ , so that they are constant. The macroscopic dissipation is, according to Eq. 72, described by the phenomenological law  $\alpha_1(X)$ , which involves the constants  $\alpha_1^{(p)}$ . *Which relations, independent of the detailed mechanism, exist that relate the  $\alpha_n^{(p)}$  for  $n > 1$  to  $\alpha_1^{(p)}$ ?* [This formulation only applies if the  $\alpha_n(X)$  are independent of  $\Omega$ . If they contain also higher powers of  $\Omega^{-1}$  (see Eq. 74), the question is: Which relations exist relating the  $\alpha_{n,\nu}^{(p)}$  for  $n > 1$  and the  $\alpha_{1,\nu}^{(p)}$  for  $\nu > 0$  to the phenomenological coefficients  $\alpha_{1,0}^{(p)}$ ?

Since this question has not been fully solved we shall only make some remarks. First, one knows that  $\Pi^{eq}(x) = \text{const.} \exp(-\frac{1}{2}x^2)$  must be a solution to each order of  $\Omega$ . By substituting this solution in Eq. 73, one obtains a relation between the coefficients of each separate order of  $\Omega$ . In particular, the order  $\Omega^0$  yields  $\alpha_2^{(0)} = -2\alpha_1^{(1)}$ , which is the familiar Nyquist relation (77). Secondly, it is possible to obtain additional relations by using the reciprocity relation (56). It has been shown for a generalized Rayleigh model (a piston between two different arbitrary mixtures of

<sup>13</sup>It may seem that the F-P equation (14) is superior in this respect to the Langevin equation, because it does not permit one to compute higher moments. The fact is, however, that some specific assumptions have been incorporated in Eq. 14 by omitting the higher derivatives. These assumptions correspond to a set of specific assumptions concerning the stochastic behavior of  $\kappa(t)$ ; they may be written in condensed form as follows:

$$\left\langle \exp \left[ \int_0^t \kappa(t') dt' \right] \right\rangle = \exp \left[ \frac{1}{2} \Gamma t \right].$$

gases) that in this way all coefficients up to order  $\Omega^{-1/2}$  are uniquely determined in terms of the coefficients  $\alpha'_{1,0}$  and  $\alpha''_{1,0}$  of the phenomenological law (Alkemade *et al.*, 1963). This is no longer true for the coefficients of the terms of order  $\Omega^{-1}$ .

## 4 Microscopic Theories

Section 3 was based on the master equation (48), which can be derived from the microscopic equations of motion (either classical or quantum-mechanical) at the expense of a repeated randomness assumption (*cf.* Section 3.1). In the present Section 4 we discuss the attempts that have been made to derive the properties of nonlinear fluctuations directly from the microscopic equations. The author believes that this easily leads to an erroneous identification of microscopic expressions with phenomenologically observed quantities, as will be pointed out in connection with the Nyquist relation for nonlinear systems.

### 4.1 Classical Theory

Let  $X$  denote a point in  $6\mathcal{N}$ -dimensional phase space,  $H(X)$  the Hamiltonian function of the isolated system, and  $\rho(X)$  a probability density describing the state of an ensemble at  $t = 0$ . The probability for some physical quantity  $Q(X)$  to lie between  $q$  and  $q + dq$  is

$$P(q, 0) dq = dq \int \delta\{Q(X) - q\} \rho(X) dX.$$

After a time  $t$ , the motion in phase space has carried  $X$  to a new point  $X^t$ , so that

$$P(q, t) = \int \delta\{Q(X^t) - q\} \rho(X) dX.$$

Equilibrium is described by

$$\rho^{eq}(X) = Z^{-1} e^{-\beta H(X)}, \quad Z = \int e^{-\beta H(X)} dX.$$

The autocorrelation function of equilibrium fluctuations is

$$\int Q(X) Q(X^t) \rho^{eq}(X) dX - \left\{ \int Q(X) \rho^{eq}(X) dX \right\}^2. \quad (78)$$

A state in which the quantity  $Q$  is known to have the value  $q_0$  is described by

$$\rho_{q_0}(X) = Z_{q_0}^{-1} e^{-\beta H(X)} \delta\{Q(X) - q_0\}, \quad (79)$$



where the normalizing factor is easily seen to be  $Z_{q_0} = ZP^{eq}(q_0)$ . The transition probability in time  $t$  is

$$P_t(q|q_0) = \int \delta\{Q(X^t) - q\} \rho_{q_0}(X) dX. \quad (80)$$

In a series of papers, Magalinskii and Terletskii (1958, 1959, 1960; Terletskii, 1958; Magalinskii, 1959) have developed this formalism. On substituting Eq. 79 in Eq. 80 and replacing the  $\delta$ -functions with their Fourier integrals, they obtain

$$P_t(q|q_0)P^{eq}(q_0) = (2\pi)^{-2} Z^{-1} \int \int \exp[i\xi q + i\xi_0 q_0] M_t(\xi|\xi_0) d\xi d\xi_0, \\ M_t(\xi|x_0) = \int \exp[-i\xi Q(X^t) - i\xi_0 Q(X)] e^{-\beta H(X)} dX.$$

This function  $M_t(\xi|\xi_0)$  contains all information concerning the quantity  $Q$ ; *e.g.*, the autocorrelation function (78) is

$$\langle QQ(t) \rangle^{eq} - \langle Q \rangle^{eq} = - \left[ \frac{\partial^2 \log M_t(\xi|\xi_0)}{\partial \xi \partial \xi_0} \right]_{\xi=\xi_0=0}. \quad (81)$$

One may also verify

$$\langle Q(t) \rangle_{q_0} = \int Q(X^t) \rho_{q_0}(X) dX \quad (82) \\ = \left[ i \frac{\partial}{\partial \xi} \log \int \exp[i\xi_0 q_0] M_t(\xi|\xi_0) d\xi_0 \right]_{\xi_0=0}.$$

Equation (80) describes an ensemble for which  $Q$  has the *precise* value  $q_0$  with no fluctuations around it. If it is only known that the *average* value  $\langle Q \rangle$  equals  $q_0$ , other choices are possible. In the spirit of Gibbs, it is natural to choose

$$\rho_{\alpha_0}(X) = Z(\alpha_0)^{-1} \exp[-\beta H(X) - \alpha_0 Q(X)], \\ Z(\alpha_0) = \int \exp[-\beta H(X) - \alpha_0 Q(X)] dX, \quad (83)$$

where  $\alpha_0$  is an auxiliary parameter, to be determined from

$$q_0 = \int Q(X) \rho_{\alpha_0}(X) dX = - \frac{\partial \log Z(\alpha_0)}{\partial \alpha_0}.$$

Alternatively, one may regard  $\rho_{\alpha_0}(X)$  as the equilibrium distribution for a new Hamiltonian  $H' = H + (\alpha_0/\beta)Q$ . This may be interpreted as the addition of an external force  $F = \alpha_0/\beta$  acting on the

coordinate  $Q$ . Hence, if the system has reached equilibrium under the influence of this constant force, and if this force is suddenly switched off at  $t = 0$ ,

$$\langle Q(t > 0) \rangle_{\alpha_0} = \int Q(X^t) \rho_{\alpha_0}(X) dX \\ = \left[ i \frac{\partial \log M_t(\xi| -i\alpha_0)}{\partial \xi} \right]_{\xi=0}. \quad (84)$$

The fact that this differs from Eq. 4.1 clearly shows that the value of  $\langle Q \rangle_t$  not only depends on the initial average  $\langle Q \rangle_0$ , but is also influenced by the fluctuations in the initial state.

If one disregards this influence, and (arbitrarily) identifies Eq. 84 with the phenomenological behavior, one arrives at an expression for  $\partial \log M_t / \partial \xi$  as a function of  $\alpha_0$  and hence of  $\xi_0$ , but only at  $\xi = 0$ . In order to extend this to other values of  $\xi$ , Magalinskii and Terletskii introduce

$$M_t(\xi - i\alpha|\xi_0 - i\alpha_0) = \int \exp[-i\xi Q(X^t) - i\xi_0 Q(X)] \times \\ \times \exp[-\beta H(X) - \alpha_0 Q(X) - \alpha_0 Q(X^t)] dX,$$

and assert that this describes the behavior of a system that at  $t = 0$  has reached equilibrium under the influence of the external force  $(\alpha_0 + \alpha)/\beta$ , which at  $t = 0$  is suddenly reduced to  $\alpha/\beta$ . This is incorrect, however, because the external force  $\alpha/\beta$  should also affect the connection between  $X^t$  and  $X$ . Indeed, the knowledge of  $M_t(\xi|\xi_0)$  is equivalent to a complete solution of the microscopic equations of motion; one cannot hope to find it from phenomenological data alone.

A correct relation has been obtained by Vladimirskii (1942). By differentiating Eq. 84, and comparing the result with Eq. 81, one has

$$- \left[ \frac{\partial}{\partial \alpha_0} \langle Q(t) \rangle_{\alpha_0} \right]_{\alpha_0=0} = - \left[ \frac{\partial^2 \log M_t(\xi|\xi_0)}{\partial \xi \partial \xi_0} \right]_{\xi=\xi_0=0} \\ \langle QQ(t) \rangle^{eq} - (\langle Q \rangle^{eq})^2. \quad (85)$$

This constitutes an exact relationship between dissipation and equilibrium fluctuations. The dissipative term on the left, however, should be carefully interpreted. It is the difference between  $\langle Q(t) \rangle$  measured for two differently prepared systems: one being in equilibrium at all times, the other having been up till  $t = 0$  in equilibrium subject to an infinitesimal external force  $F = \alpha_0/\beta$ , which is then switched off.

## 4.2 The Quantum Mechanical Theory of Bernard and Callen

Let  $H$  be the Hamiltonian of a closed, isolated system,  $Z = \text{Tr} e^{-\beta H}$  its partition function, and

$\rho^{eq} = Z^{-1}e^{-\beta H}$  the density matrix describing equilibrium. If  $Q$  is the operator associated with a certain physical quantity in the Schrödinger representation, then variation of this quantity in time is described by the Heisenberg operator

$$Q(t) = e^{itH}Qe^{-itH} \quad (\hbar = 1). \quad (86)$$

It is natural to take as a quantum mechanical version of the autocorrelation function (7)

$$\frac{1}{2}\langle QQ(t) + Q(t)Q \rangle^{eq} = \frac{1}{2}\text{Tr}\rho^{eq}\{QQ(t) + Q(t)Q\}. \quad (87)$$

If the subscripts  $k, l, \dots$  denote the various eigenstates of the exact Hamiltonian  $H$ , and  $E_k$  its eigenvalues, the expression (87) may be written

$$\frac{1}{2}Z^{-1}\sum_{k,l}e^{-\beta E_k}Q_{kl}Q_{lk}\{e^{it(E_l-E_k)} + e^{-it(E_l-E_k)}\}.$$

The spectral density of the fluctuations is, according to the Wiener-Khintchine theorem (10),

$$S_Q(\omega) = Z^{-1}\sum_{k,l}e^{-\beta E_k}|Q_{kl}|^2 \times \{\delta(E_k - E_l + \omega) + \delta(E_k - E_l - \omega)\}.$$

By interchanging the subscripts  $k$  and  $l$  in the second term, one obtains

$$S_Q(\omega) = Z^{-1}(1 + e^{-\beta\omega})\sum_{k,l}e^{-\beta E_k}|Q_{kl}|^2\{\delta(E_k - E_l + \omega)\}. \quad (88)$$

It is less clear how the phenomenological law is connected with the microscopic quantum mechanical formalism. We shall here describe the method of Bernard and Callen (1959). Let  $F$  be an external force acting on  $Q$ , such that the Hamiltonian is  $H + FQ$ . It is argued that  $F$  may be regarded as a known complex number depending on time. The density matrix  $\rho(t)$  obeys the equation

$$i\dot{\rho} = [H, \rho] + F(t)[Q, \rho]. \quad (89)$$

One splits off the unperturbed part of  $\rho$ , putting

$$\rho = \rho^{eq} + e^{-itH}\sigma e^{itH},$$

so that

$$i\dot{\sigma} = F(t)[Q(t), \rho^{eq}] + O(F^2).$$

Supposing that at  $t = -\infty$  the system is in the unperturbed equilibrium state described by  $\rho^{eq}$ , one has to first order in  $F$ ,

$$\sigma(t) = -i\int_{-\infty}^t F(t')[Q(t'), \rho^{eq}]dt'. \quad (90)$$

Hence, the expectation value of  $Q$  at time  $t$  is

$$\langle Q \rangle_t = \langle Q \rangle^{eq} + i\int_{-\infty}^t F(t')dt'\text{Tr}\rho^{eq}[Q(t'), Q(t)]. \quad (91)$$

Let the “aftereffect function”  $\Phi(t_2 - t_1)$  be defined for  $t_2 \geq t_1$  as the response  $\langle Q \rangle$  at  $t_2$ , provoked by a pulse  $F(t) = \delta(t - t_1)$ . According to Eq. 91

$$\Phi(t_2 - t_1) = i\text{Tr}\rho^{eq}[Q(t_1)Q(t_2)] = i\langle [Q, Q(t_2 - t_1)] \rangle^{eq}.$$

The response to the periodic force  $F(t) = e^{i\omega t}$  is  $\langle Q \rangle_t - \langle Q \rangle^{eq} = L(\omega)e^{-\omega t}$ , where the “response function” is

$$L(\omega) = \int_0^{\infty} \Phi(t)e^{i\omega t}dt. \quad (92)$$

A similar calculation as used above yields

$$\text{Im}L(\omega) = -\pi Z^{-1}(1 + e^{-\beta\omega}) \times \sum_{k,l}e^{-\beta E_k}|Q_{kl}|^2\{\delta(E_k - E_l + \omega)\}.$$

Comparison with Eq. 88 leads to a relation between this response function and the fluctuation spectrum:

$$S_Q(\omega) = -\frac{1}{\pi} \frac{1 + e^{-\beta\omega}}{1 - e^{-\beta\omega}} \text{Im}L(\omega). \quad (93)$$

This is the “fluctuation-dissipation theorem” (Callen and Welton, 1951). As an example: when this relation is applied to the electric circuit of Fig. 1 (with constant resistance  $R$ ), one has  $F = V/R$ ,  $L(\omega) = -R^{-1}(-i\omega + 1/RC)^{-1}$  so that one finds Eq. 11 as the classical limit ( $\beta\omega \ll 1$ ).

Subsequently, Bernard and Callen proceed to the next order, which involves three effects.

- i. The response (90) is supplemented by a term of order  $F^2$ :

$$- \int_{-\infty}^t F(t')dt' \int_{-\infty}^{t'} F(t'')dt''\text{Tr}\rho^{eq}\{Q(t''), [Q(t'), Q(t)]\}. \quad (94)$$

- ii. In a stationary state with constant driving force  $F$ , the fluctuation spectrum is no longer equal to Eq. 88. The correction is now taken into account to first order in  $F$ . It clearly involves products of three factors  $Q$  and is therefore related to the double commutator in Eq. 94.
- iii. Even in equilibrium, the autocorrelation function (88) is not an exhaustive description of the stochastic properties of the fluctuations; more information is contained in the higher moments. The third moment  $\langle \{QQ(t)Q(t')\}_{\text{symmetrized}} \rangle^{eq}$  belongs to the same approximation as the above effects (i) and (ii).

We shall not discuss these higher order terms, however, because a serious difficulty appears already in Eq. 93. This equation asserts that the fluctuation spectrum in equilibrium is completely determined by the linear response alone, regardless of the existence of nonlinear terms in the phenomenological response. This contradicts our previous results, in particular Eq. 44, for the diode model. The point will be discussed presently.

We stress the fundamental difference between the approaches in this section and in the previous one. The previous section is based on the master equation (48), which describes the stochastic behavior of a macroscopic variable. The stochastic character, together with irreversibility, is due to the repeated averaging over all other microscopic variables, see Section 3.1. The present section is directly based on the microscopic equation of motion, without averaging over microscopic variables.<sup>14</sup> As a consequence, Eq. 91 expresses  $\langle Q \rangle_t$  as an integral over the entire past of  $F(t)$ . The system never forgets, because no irreversibility has entered the picture. This is clearly exhibited by the fact that, in addition to Eq. 91, one has the anticausal equation

$$\langle Q \rangle_t = \langle Q \rangle^{eq} - i \int_t^\infty F(t') dt' \text{Tr} \rho^{eq} [Q(t'), Q(t)],$$

if it supposed that the system is in equilibrium at  $t = +\infty$ . Accordingly Eq. 91 is of entirely different nature than Eqs. 1 and 2, which express the rate of change of  $Q$  in terms of the instantaneous value of the force.

<sup>14</sup>The density matrix implies an averaging over initial states, but that is a more elementary process, which does not suffice to derive the ME.

In a second paper, Bernard and Callen (1960) support their conclusion that the fluctuation spectrum is not affected by nonlinear terms, without invoking the microscopic equations. However, they here start from Eq. 15, which was shown by Polder to be untenable. This is related to the fact that the expression they use for the autocorrelation function is incorrect (van Kampen, 1960).

### 4.3 An Alternative Quantum Mechanical Treatment; Discussion

Stratonovich (1960) has quantized the theory of Magalinskii and Terletskii (Section 4.1); we merely reproduce the main results. A state given by  $\langle Q \rangle$  is described by the density matrix

$$\begin{aligned} \rho_{\alpha_0} Z(\alpha_0)^{-1} \exp(-\beta H - \alpha_0 Q), \\ Z(\alpha_0) = \text{Tr} \exp(-\beta H - \alpha_0 Q), \end{aligned} \quad (95)$$

which is the quantum analog of Eq. 83. Let us introduce again the auxiliary function

$$M_t(\xi|\xi_0) = \text{Tr} \exp(-\beta H - i\xi_0 Q) e^{-i\xi Q(t)},$$

where  $Q(t)$  is the same as in Eq. 86. Then one has

$$\langle Q(t) \rangle_{\alpha_0} = \text{Tr} \rho_{\alpha_0} Q(t) = \left[ i \frac{\partial \log M_t(\xi| -i\alpha_0)}{\partial \xi} \right]_{\xi=0},$$

in complete analogy with Eq. 84.

In order to find the analog of Eq. 81, one needs the identity

$$\begin{aligned} \frac{\partial}{\partial \xi_0} \exp(-\beta H - i\xi_0 Q) = \\ \frac{-i}{\beta} e^{-\beta H} \int_0^\beta e^{\beta' H} Q e^{-\beta' H} d\beta' + O(\xi_0). \end{aligned}$$

It is then easy to compute

$$\left[ \frac{\partial^2 M_t(\xi|\xi_0)}{\partial \xi \partial \xi_0} \right]_{\xi=\xi_0=0} = -\frac{1}{\beta} \int_0^\beta d\beta' \text{Tr} \{ e^{-\beta H} Q Q(t + i\beta') \}.$$

Hence one finds, instead of the classical Eq. 81,

$$\begin{aligned} - \left[ \frac{\partial^2 \log M_t(\xi|\xi_0)}{\partial \xi \partial \xi_0} \right]_{\xi=\xi_0=0} = \\ = \frac{1}{\beta} \int_0^\beta d\beta' \{ \langle Q Q(t + i\beta') \rangle^{eq} - (\langle Q \rangle^{eq})^2 \} \\ = \left( i\beta \frac{d}{dt} \right)^{-1} \left\{ \exp \left[ i\beta \frac{d}{dt} \right] - 1 \right\} \{ \langle Q Q(t) \rangle^{eq} - (\langle Q \rangle^{eq})^2 \}. \end{aligned}$$

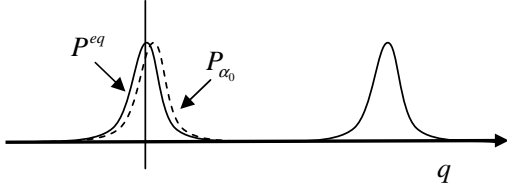


Figure 7: **The equilibrium distribution  $P^{eq}$ , the shifted distribution  $P_{\alpha_0}$ , and a distribution that appears to a macroscopic observer as a non-equilibrium state.**

Thus, the second derivative of  $M_t$  is no longer identical with the autocorrelation function, but an operator intervenes acting on the time dependency. Accordingly, one now obtains instead of Eq. 85

$$\begin{aligned} & \langle QQ(t) \rangle^{eq} - \langle \langle Q \rangle^{eq} \rangle^2 = \\ & = \left( i\beta \frac{d}{dt} \right) \left\{ \exp \left[ i\beta \frac{d}{dt} \right] - 1 \right\}^{-1} \left[ \frac{\partial}{\partial \alpha_0} \langle Q(t) \rangle_{\alpha_0} \right]. \end{aligned}$$

The real part of this equation is (take  $\langle Q \rangle^{eq} = 0$  for brevity)

$$\begin{aligned} & \frac{1}{2} \langle QQ(t) + Q(t)Q \rangle^{eq} = \quad (96) \\ & = - \left( \frac{\beta}{2} \frac{d}{dt} \right) \cot \left( \frac{\beta}{2} \frac{d}{dt} \right) \left[ \frac{\partial \langle Q(t) \rangle_{\alpha_0}}{\partial \alpha_0} \right]_{\alpha_0=0}. \end{aligned}$$

To show that this result is identical with Eq. 93, we first note that  $\langle Q(t) \rangle_{\alpha_0}$  is the aftereffect of a constant force  $F = \alpha_0/\beta$ , acting from  $t = -\infty$  till  $t = 0$ ,

$$\langle Q(t) \rangle_{\alpha_0} = \int_{-\infty}^0 \Phi(t-t') \frac{\alpha_0}{\beta} dt' + O(\alpha_0^2).$$

Hence,

$$\left[ \frac{\partial}{\partial \alpha_0} \langle Q(t) \rangle_{\alpha_0} \right]_{\alpha_0=0} = \frac{1}{\beta} \int_t^{\infty} \Phi(t') dt'.$$

Substitute this in Eq. 96, multiply with  $(2/\pi) \cos \omega t$ , integrate from  $-\infty$  to 0: the result is Eq. 93.

Equation (85), its quantum mechanical version (96), and the Fourier transform thereof, Eq. 93, are equivalent expressions of the relation between equilibrium fluctuations and the relaxation of  $\langle Q \rangle$  after a weak force has been applied. We shall argue that this relaxation is *not* identical with macroscopic dissipation, except perhaps in the linear case. The quantities

$\Phi(t)$ ,  $L(\omega)$ , and  $[(\partial/\partial \alpha_0) \langle Q(t) \rangle_{\alpha_0}]_{\alpha_0=0}$  all refer to the range in which the *microscopic* motion depends linearly on  $F$ . A rough estimate shows that this requires  $F$  to be incredibly weak, in particular when it acts during a long time period. It is not true that the first-order solution of the microscopic equations, such as Eq. 90, is a valid approximation in the same range in which the phenomenological law is linear, as is often taken for granted (Weber, 1956). Hence the nonequilibrium distribution  $\rho_{\alpha_0}$  [Eqs. 83 or 95] must be a probability distribution that is only very slightly shifted away from equilibrium (Fig 7). The quantities calculated in the present chapter refer to the relaxation of such a slightly shifted distribution, to first order in the shift  $\alpha_0$ . The phenomenological law, however, refers to relaxation of a quite different distribution which is much further removed from equilibrium, so far that it does not overlap at all and that the first order in  $\alpha_0$  is meaningless.

In order to exhibit more explicitly the difference between these two aspects, we derive the equivalent of Eq. 85 using the approach of Section 3. On the one hand, the autocorrelation function is given by Eq. 7, and we suppose again  $\langle q \rangle^{eq} = 0$ . On the other hand, take an ensemble whose initial state is the shifted distribution

$$P(q, 0) = P_{\alpha_0}(q) = (2\pi)^{-1/2} \exp(-\frac{1}{2} \alpha_0^2) \exp(-\frac{1}{2} q^2 - \alpha_0 q).$$

If this is expanded in  $\alpha_0$

$$P_{\alpha_0}(q) = P^{eq}(q)[1 - \alpha_0 q + \dots] \quad (97)$$

one has

$$\begin{aligned} \langle q(t) \rangle &= \int \int q dq P_t(q|q_0) P(q_0, 0) dq_0 \\ &= -\alpha_0 \langle q(0)q(t) \rangle^{eq} + O(\alpha_0^2), \quad (98) \end{aligned}$$

which is identical with Vladimirkii's equation (85).

This derivation shows clearly that the result does apply to nonlinear systems, since no specific form for  $P_t(q|q_0)$  has been used. It also shows that the linearity in  $\alpha_0$  is obtained through Eq. 97, which implies that the external force must be so weak that the shift in  $q$  is much smaller than the fluctuations. This condition is certainly not fulfilled by a state that differs macroscopically from the equilibrium state. One is not justified, therefore, in identifying the coefficient of  $\alpha_0$  in Eq. 98 with the first coefficient of the nonlinear phenomenological law. A further investigation of this point seems to me essential for the correct understanding of nonlinear systems.

## References

- Alkemade, C. T. J. (1958) *Physica* **24**, 1029.
- Alkemade, C. T. J., van Kampen, N. G., and MacDonald, D. K. C. (1963) *Proc. Roy. Soc.* **A271**, 449.
- Bernard, W., and Callen, H. B. (1959) *Rev. Mod. Phys.* **31**, 1017.
- Bernard, W., and Callen, H. B. (1960) *Phys. Rev.* **118**, 1466.
- Brillouin, L. (1950) *Phys. Rev.* **78**, 627.
- Brinkman, H. C. (1957) *Physica* **23**, 82.
- Brinkman, H. C. (1958) *Physica* **24**, 409.
- Burgess, R. E. (1955a) *Proc. Phys. Soc. (London)* **B68**, 661.
- Burgess, R. E. (1955b) *Brit. J. Appl. Phys.* **6**, 185.
- Burgess, R. E. (1956) *Proc. Phys. Soc. (London)* **B69**, 1020.
- Callen, H. B., and Welton, T. A. (1951) *Phys. Rev.* **83**, 34.
- Davies, R. O. (1958) *Physica* **24**, 1055.
- Deutsch, R. (1952) "Nonlinear Transformations of Random Processes." Prentice Hall, Englewood Cliffs, New Jersey.
- Einstein, A. (1905) *Ann. Physik* **17**, 549.
- Einstein, A. (1906) *Ann. Physik* **19**, 371.
- Fokker, A. D. (1913) Thesis, Leiden.
- Fokker, A. D. (1914) *Ann. Physik* **43**, 810.
- Khintchine, A. (1933) *Ergeb. Math.* **2** (4).
- Kramers, H. A. (1940) *Physica* **7**, 284.
- Lax, M. (1960) *Rev. Mod. Phys.* **32**, 25.
- MacDonald, D. K. C. (1954) *Phil. Mag.* **45**, 63, 345.
- MacDonald, D. K. C. (1957) *Phys. Rev.* **108**, 541.
- Magalinskii, V. B. (1959) *Zh. Eksperim. i Teor. Fiz.* **36**, 1423; *Soviet Phys. JETP (English Transl.)* **9**, 1011.
- Magalinskii, V. B., and Terletskii, I. P. (1958) *Zh. Eksperim. i Teor. Fiz.* **34**, 729; *Soviet Phys. JETP* **7**, 501.
- Magalinskii, V. B., and Terletskii, I. P. (1959) *Zh. Eksperim. i Teor. Fiz.* **36**, 1731; *Soviet Phys. JETP* **9**, 1234.
- Magalinskii, V. B., and Terletskii, I. P. (1960) *Ann. Physik* **5**, 296.
- Marek, A. (1959) *Physica* **25**, 1358.
- Middleton, D. M. (1951) *J. Appl. Phys.* **22**, 1143, 1153.
- Middleton, D. M. (1960). "An Introduction to Statistical Communication Theory," McGraw-Hill, New York.
- Mott, N. F., and Gurney, R. W. (1940). "Electronic Processes in Ionic Crystals," p. 181. Clarendon, Oxford.
- Moyal, J. E. (1949) *J. Roy. Statis. Soc.* **B11**, 150.
- Nyquist, H. (1928) *Phys. Rev.* **32**, 110.
- Planck, M. (1917) *Sitzber. Preuss. Akad. Wiss.* p. 324. (1958) "Physikalische Abhandlungen und Vorträge," F. Vieweg & Sohn, Braunschweig, Vol. II, p. 435.
- Polder, D. (1954) *Phil. Mag.* **45**, 69.
- Prigogine, I. (1962) "Non-equilibrium Statistical Mechanics." Interscience, New York.
- Rayleigh, Lord (1891) *Phil. Mag.* **32**, 424; (1902) "Scientific Papers," University Press, Cambridge, Vol. III, p. 473.
- Rytov, S. M. (1955) *Zh. Eksperim. i Teor. Fiz.* **29**, 304; *Soviet Phys. JETP* **2**, 217.
- Siegel, A. (1960) *J. Math. Phys.* **1**, 378.
- Stratonovich, R. L. (1960) *Zh. Eksperim. i Teor. Fiz.* **39**, 1647; *Soviet Phys. JETP* **12**, 1150.
- Terletskii, I. P. (1958) *Nuovo Cimento* **7**, 308.
- Uhlenbeck, G. E., and Ornstein, L. S. (1930) *Phys. Rev.* **36**, 823.
- Uhlhorn, U. (1960) *Arkiv Fysik* **17**, 361.
- van der Ziel, A. (1959) "Fluctuation Phenomena in Semiconductors." Butterworths, London.
- Van Hove, L. (1955) *Physica* **21**, 517.
- Van Hove, L. (1962) In "Fundamental Problems in Statistical Mechanics: Proceedings of the NUFFIC International Summer Course, Netherlands, 1961" (E. G. D. Cohen ed.) pp. 156–167. North-Holland, Amsterdam.
- van Kampen, N. G. (1954) *Physica* **20**, 603.
- van Kampen, N. G. (1956) *Fortschr. Physik* **4**, 405.
- van Kampen, N. G. (1957) *Physica* **23**, 707 and 816.
- van Kampen, N. G. (1958) *Phys. Rev.* **110**, 319.
- van Kampen, N. G. (1960) *Physica* **26**, 585.
- van Kampen, N. G. (1961a) *Can. J. Phys.* **39**, 551.
- van Kampen, N. G. (1961b) *J. Math. Phys.* **2**, 592.
- van Kampen, N. G. (1962) In "Fundamental Problems in Statistical Mechanics: Proceedings of the NUFFIC International Summer Course, Netherlands, 1961" (E. G. D. Cohen ed.) pp. 173–202. North-Holland, Amsterdam.
- Vladimirskii, V. V. (1942) *J. Exptl. Theoret. Phys. (U. S. S. R.)* **12**, 199; quoted by Stratonovich (1960).
- Weber, J. (1956) *Phys. Rev.* **101**, 1620.
- Wigner, E. P. (1954) *J. Chem. Phys.* **22**, 1912.
- Zernike, F. (1929) *Handbuch der Physik* **3**, 419.