# Phenomenological approach to nonlinear Langevin equations

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In this paper we address the problem of consistently constructing Langevin equations to describe fluctuations in nonlinear systems. Detailed balance severely restricts the choice of the random force, but we prove that this property, together with the macroscopic knowledge of the system, is not enough to determine all the properties of the random force. If the cause of the fluctuations is *weakly* coupled to the fluctuating variable, then the statistical properties of the random force can be completely specified. For variables odd under time reversal, microscopic reversibility and weak coupling impose symmetry relations on the variable-dependent Onsager coefficients. We then analyze the fluctuations in two cases: Brownian motion in position space and an asymmetric diode, for which the analysis based in the master equation approach is known. We find that, to the order of validity of the Langevin equation proposed here, the phenomenological theory is in agreement with the results predicted by more microscopic models.

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#### I. INTRODUCTION

A widely used method to study fluctuations is the socalled Langevin approach, introduced by Langevin [1] as a way to study Brownian motion [2,3]. In his treatment, the interaction force between the Brownian particle and the bath particles is split into two contributions. The first one corresponds to the damping due to the frictional force exerted by the bath. The second one arises from the thermal motion of the bath molecules. The Brownian particle then experiences a large number of collisions per unit of time with the bath molecules, which give rise to a rapidly varying contribution, responsible for the observed erratic motion of the particle. Then, the equation for the velocity of a Brownian particle of unit mass can be written as

$$\dot{u}(t) = -\xi u(t) + F(t) . \qquad (1.1)$$

The first term of the right-hand side is the friction force. This force is a linear function of the variable  $u, \xi$  being the friction coefficient. The second term stands for the Langevin *complementary* force or random force, whose nature is unknown a priori. Beyond Langevin's original treatment and with the aim of determining u(t), several assumptions have been made on the nature of the random force. The most basic one is that F(t), being an unpredictable rapidly varying function of time, is taken as a stochastic process, often assumed to be Gaussian and white with zero mean [2]. The second moment of F(t) is determined by means of the fluctuation-dissipation theorem, which relates the strength of the random force to the dissipation, i.e., the friction coefficient,  $\xi$ . This crucial point ensures that the law of equipartition of energy is satisfied by the system under the effect of F(t). With all these assumptions, the statistical properties of the random variable u(t) can be obtained [2].

Let us consider here a generic macroscopic variable, X(t), whose relaxation is phenomenologically described by the equation

$$\dot{X}(t) = -A(X(t)) , \qquad (1.2)$$

where A(X(t)) is the flux of the variable which can be a nonlinear function of X(t). In this paper, we will be interested in the dynamics of the fluctuations of that variable. The fluctuating counterpart of X(t) will be denoted by x(t), the former being obtained from the latter by some averaging procedure. It has been then proposed that x(t)satisfies the equation

$$\dot{x}(t) = -A(x(t)) + F(t)$$
 (1.3)

obtained by replacing X(t) by x(t) in the phenomenological equation (1.2) and adding a Langevin force, assumed to be Gaussian and white. This approach has been used for systems in which A(x) is a linear function of the variable x [4-6]. However, when A(x) is nonlinear, the addition of a random force F(t) to Eq. (1.2), as a procedure to describe the random process x(t), has often been questioned. We want to emphasize two main criticisms [7]:

(i) The Gaussian nature of the random process F(t) is postulated [2], but a more general character of the process could in principle be equally plausible.

(ii) Averaging Eq. (1.3) with respect to the realizations of the F(t) given an initial condition  $x_0$ , identifying X(t)with  $\langle x(t) \rangle_{x_0}$ , and comparing with the phenomenological equation (1.2), one finds that

$$\langle A(x(t)) \rangle_{x_0} \neq A(X(t))$$
 (1.4)

if A(x) is not a linear function of x. It is then argued that this difference arises from the fact that the use of A(x) also in the equation for the fluctuations (1.3) is

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not justified because A(x) is phenomenological, that is, it is known except a function of the order of the strength of the fluctuations. (See also the comments in Ref. [9] about this point.) In view of these criticisms, it is often concluded that the Langevin approach is not valid for the case of internal (thermal) noise in nonlinear systems and that a more microscopic description is necessary to derive the proper equation for the fluctuations [8].

Recently, however, some attention has been paid to the properties of the Langevin random force in the case of thermal noise for a physical system bearing a nonlinear A(x). Let us write A(x) under the form

$$A(x) \equiv -\beta(x)\frac{d}{dx}\ln P_e(x) , \qquad (1.5)$$

where  $P_e(x)$  is the equilibrium probability density of the variable x, supposed known, and  $\beta(x)$  is a given function of x. Equation (1.5) emphasizes the fact that the macroscopic flux is a function of the thermodynamic force

$$\mathcal{F}(x) = rac{\partial}{\partial x} \ln P_e(x)$$
 (1.6)

such that the flux vanishes when the thermodynamic force also vanishes. Near equilibrium,  $\beta$  tends to a constant and A(x) takes the form of a linear function of the thermodynamic force  $\mathcal{F}$ , in the spirit of Onsager's theory of irreversible processes. Thus,  $\beta(x)$  is the corresponding variable-dependent Onsager coefficient. Mazur and Bedeaux have proved that the underlying microscopic reversibility, when applied to the Langevin equation, severely restricts the properties of the Langevin complementary force, contrary to what is stated in the first remark. Indeed, if x(t) in Eq. (1.3) is a variable even or odd under time-reversal and if F(t) is independent of the variable x(t), it is found that [9] (1) F(t) must be a Gaussian process and (2)  $\beta(x)$  must be a constant. Note that if  $P_e(x)$  is not Gaussian, then A(x) is nonlinear even if  $\beta$  is a constant and, however, F(t) still must be a Gaussian process. Furthermore, another conclusion that can be drawn from this result is that if  $\beta(x)$  is not a constant, F(t) cannot be independent of x(t). This case will be referred to as *genuinely* nonlinear.

A simple way to construct a random force depending on the variable x(t) is to assume that [10,11]

$$F(t) = \tilde{c}(x(t))\tilde{L}(t) \tag{1.7}$$

often referred to as multiplicative noise. Here,  $\tilde{L}(t)$  is a stationary white process, independent of x(t) and  $\tilde{c}(x)$  is a given nonvanishing function of x.

In general, when proposing a Langevin equation to study thermal fluctuations in a given system, one would wish that the properties of the random force would follow from the phenomenological knowledge of the system. It is clear, as claimed in Ref. [3], that if a detailed microscopic description is available, there are ways to derive the equation for the fluctuations of a given variable without ambiguity. However, we are interested in the situations where this information is lacking, although it will be assumed that there exists an underlying microscopic description in terms of Hamilton or Schrödinger equations, and that a relation like Eq. (1.2) is known. The aim of this paper is to use the information at hand to consistently determine a Langevin equation for x(t)in the genuinely nonlinear case. To this end and in the same spirit as in Refs. [9-11], we will use generally valid properties such as microscopic reversibility to fix the nature of the random force. Furthermore, we will discuss the range of applicability of the theory developed. To that purpose, we will consider that the equation for the evolution of x(t) is given again by the phenomenological law (1.2) plus two additional contributions. The first one is a variable-dependent random force,  $\tilde{F}((xt), t)$ , defined by

$$\tilde{F}(x(t),t) \equiv \int dx \delta(x-x(t)) \tilde{L}(x,t) ,$$
 (1.8)

where  $\tilde{L}(x,t)$  is a stationary and white random process, depending on a parameter x but independent of random process x(t), which is characterized by its cumulants [3]

$$\langle \tilde{L}(x,t) \rangle_c = 0 , \qquad (1.9)$$

$$\langle L(x_1, t_1)L(x_2, t_2)\rangle_c = \tilde{c}_2(x_1, x_2)\delta(t_1 - t_2) , \qquad (1.10)$$

$$\langle \tilde{L}(x_1, t_1) \tilde{L}(x_2, t_2) \cdots \tilde{L}(x_n, t_n) \rangle_c = \tilde{c}_n(x_1, x_2, \dots, x_n) \delta(t_n - t_1) \delta(t_n - t_2) \cdots \delta(t_n - t_{n-1}) .$$
(1.11)

Note that while L(x,t) is independent of the process x(t), the statistical properties of  $\tilde{F}(x(t),t)$  will depend on the evolution equation for x(t).

The second contribution is a function  $\tilde{\Gamma}(x)$ , standing for a possible modification of the phenomenological flux A(x) due to fluctuations. The proposed Langevin equation then reads

$$\dot{x}(t) = -A(x(t)) + \tilde{\Gamma}(x(t)) + \tilde{F}(x(t),t) . \qquad (1.12)$$

A priori, both  $\tilde{\Gamma}(x)$  and the set of functions  $\tilde{c}_i(\{x_i\})$  are undetermined. We will specialize in the simplest,

although very important, case in which the random process L(x,t) depends only on one single function c(x), all the cumulants present in Eqs. (1.9)-(1.11) being related with c(x). This case will be later identified with the widely used multiplicative noise [10,11]. The general case will be analyzed elsewhere. The presence of the unknown function  $\tilde{\Gamma}(x)$  in Eq. (1.12) as well as the treatment to be developed are the main differences with respect to the analysis given in Refs. [9–11], permitting a larger degree of freedom with important consequences.

The paper is organized as follows. In the next section we will obtain the master equation for the one-

dimensional process x(t) described by Eq. (1.12) with multiplicative noise. In Sec. III we apply detailed balance to the master equation to show that  $\tilde{L}(x,t)$  needs to be Gaussian, which constitutes an alternative derivation of the results of Ref. [11]. In addition, we will also obtain a differential equation involving  $\tilde{c}(x)$  and  $\tilde{\Gamma}(x)$ , as well as the symmetries imposed to these functions, reminiscent of the Onsager symmetry relations. In our context, such an equation serves to fix neither  $\tilde{c}(x)$  nor  $\tilde{\Gamma}(x)$  but it is a mere relationship between them. This suggests that detailed balance alone is not enough to unequivocally determine the properties of the additional terms in Eq. (1.12). In Sec. IV, we will analyze Brownian motion in position space to illustrate the main ideas exposed so far. This particular example will serve us to illustrate that if the mechanisms causing the fluctuations are weakly coupled to the fluctuating variable, then we can unequivocally determine  $\tilde{c}(x)$  and  $\tilde{\Gamma}(x)$ . This will be called the *weak* coupling assumption. In the same section, we also apply these ideas to Alkemade's diode [12,13], often used to show the failure of the phenomenological treatment of the fluctuations. This last example will permit us to analyze the phenomenological theory developed along the paper to the light of a more microscopic description and, therefore, determine its range of applicability. Section V is devoted to the conclusions and to a brief summary of the ideas sketched in this paper.

## **II. THE MASTER EQUATION**

Let us assume that the dynamics of the onedimensional variable x(t), even or odd under time reversal, is described phenomenologically, that is, in the absence of fluctuations, by Eq. (1.2). Note that this statement constitutes a definition of the phenomenological equation. For the fluctuations we have the Langevin equation given in Eq. (1.12), which we rewrite as

$$\dot{x}(t) = -\tilde{B}(x(t)) + \tilde{F}(x(t), t)$$
(2.1)

 $\mathbf{with}$ 

$$ilde{B}(x) \equiv -eta(x) rac{\partial}{\partial x} \ln P_e(x) - ilde{\Gamma}(x) \;,$$
 (2.2)

where the form (1.5) for A(x) is used. Note that the "renormalized" flux  $\tilde{B}(x)$  is not completely determined since it depends on the unknown  $\tilde{\Gamma}(x)$ . We will define an *acceptable*  $\tilde{B}(x)$  as such that, after fixing  $\tilde{\Gamma}(x)$ , it still retains some dependence on the macroscopically relevant Onsager coefficient  $\beta(x)$ .

The random force  $\tilde{F}(x(t), t)$ , as it stands in Eq. (1.8), cannot be unequivocally interpreted unless a rule to compute averages of the form  $\langle g(x(t))\tilde{L}(x,t)\rangle$ , g(x) being an arbitrary function, is provided [3]. In the literature, this ambiguity is often referred to as the Itô-Stratonovich dilemma. For causality reasons, we demand [9,10] that the state of the system at t is not correlated with the random force at the same time, that is,

$$\langle \tilde{F}(x(t),t) \rangle = \int dx \langle \delta(x-x(t)) \rangle \langle \tilde{L}(x,t) \rangle = 0 , \quad (2.3)$$

which in fact prescribes Itô's rule. However, from the mathematical point of view, the Itô-Stratonovich dilemma is immaterial in our case since  $\tilde{\Gamma}(x)$ , and the properties of  $\tilde{L}(x,t)$  are a priori unknowns that will be determined later on, on the basis of physical arguments and in agreement with the chosen interpretation rule.

For simplicity's sake, in the calculation which follows we will assume Stratonovich's rule. Then, for clarity, we introduce  $\Gamma(x)$ , F(x(t), t), L(x, t), and the cumulants  $\{c_n(x_1, \ldots, x_n)\}$ , as the quantities consistent with Stratonovich's rule while  $\tilde{\Gamma}(x)$ ,  $\tilde{F}(x(t), t)$ ,  $\tilde{L}(x, t)$ , and  $\{\tilde{c}_n(x_1, \ldots, x_n)\}$  will be those consistent with Itô's rule. Since both describe the same physical situation, we must have that the equations

 $\dot{x}(t) = -A(x(t)) + \Gamma(x) + F(x(t),t)|_{\text{Stratonovich}},$  (2.4)

$$\dot{x}(t) = -A(x(t)) + \tilde{\Gamma}(x) + \tilde{F}(x(t), t) \Big|_{\mathrm{It\hat{o}}}$$
(2.5)

are equivalent.

Assuming thus Stratonovich's rule, we introduce the multiplicative noise as the particular case in which the set of cumulants in Eqs. (1.9)-(1.11) takes the form

$$c_n(x_1, x_2, \ldots, x_n) = \alpha_n c(x_1) c(x_2) \cdots c(x_n) , \qquad (2.6)$$

 $\alpha_n$  being constants. This particular choice of the random process L(x,t) makes it equivalent to c(x)L(t) as in Eq. (1.7), with L(t) a stationary white random process whose cumulants are the set of constants  $\{\alpha_i\}$ . Note that the choice done in Eq. (2.6) does not imply a Gaussian nature of the random process L(x,t) which, in turn, is going to be Gaussian if  $\alpha_i = 0$  for  $i \geq 3$ .

To obtain the master equation for the probability, we will essentially follow Ref. [9]. Let us first consider the density distribution

$$\rho(x,t) \equiv \delta(x-x(t)) , \qquad (2.7)$$

where x(t) is the solution of Eq. (2.4) for a particular realization of L(x,t) and a given initial condition  $x_0 \equiv x(t=0)$ . Then, the conditional probability  $P(x,t|x_0)$  for the random variable x(t) to be at the point x at t, given that it was at the point  $x_0$  at t = 0, is related to  $\rho(x,t)$ by

$$P(x,t|x_0) = \langle \rho(x,t) \rangle_{x_0} , \qquad (2.8)$$

where, again, the averages are over all the realizations of L(x,t) and the subindex  $x_0$  indicates that the same initial condition  $x_0$  is considered. Clearly,

$$P(x,t=0|x_0) = \delta(x-x_0) . \qquad (2.9)$$

In Appendix A we show that  $P(x, t|x_0)$  satisfies

$$\frac{\partial}{\partial t}P(x,t|x_0) = \left[\frac{\partial}{\partial x}B(x) + \sum_{n=2}^{\infty} (-1)^n \frac{1}{n!} \alpha_n \left(\frac{\partial}{\partial x}c(x)\right)^n\right] \times P(x,t|x_0)$$
(2.10)

which is the Kramers-Moyal expansion of the master equation [3]

$$egin{aligned} &rac{\partial}{\partial t}P(x,t|x_0) = \int dx' \left[w(x'
ightarrow x)P(x',t|x_0)
ight. \ &- w(x
ightarrow x')P(x,t|x_0)
ight] \ &\equiv \int dx'\,\hat{\mathcal{W}}(x|x')P(x',t|x_0)\;. \end{aligned}$$

Here,  $w(x \to x')$  stands for the transition probability from the state x to x', and the operator  $\hat{\mathcal{W}}(x|x')$  is defined as

$$\hat{\mathcal{W}}(x|x')\equiv w(x'
ightarrow x)-\delta(x-x')\int dx''\,w(x
ightarrow x'')\;.$$

Equation (2.10) can be expressed in a more compact form by introducing the operator  $\hat{\mathcal{L}}(x)$ :

$$\hat{\mathcal{L}}(x) \equiv \frac{\partial}{\partial x} B(x) + \sum_{n=2}^{\infty} (-1)^n \frac{1}{n!} \alpha_n \left(\frac{\partial}{\partial x} c(x)\right)^n . \quad (2.13)$$

Then

$$\frac{\partial}{\partial t}P(x,t|x_0) = \hat{\mathcal{L}}(x)P(x,t|x_0) . \qquad (2.14)$$

We thus identify

$$\hat{\mathcal{W}}(x|x') = \hat{\mathcal{L}}(x)\,\delta(x-x') \,. \tag{2.15}$$

Furthermore, due to the Markovian nature of the process under discussion, we can write

$$P(x,t) = \int dx' P(x,t|x',t') P(x',t') , \qquad (2.16)$$

where P(x,t) is the one-point probability density. Setting  $x' = x_0$  and t' = 0 in this last equation, multiplying both sides of Eq. (2.14) by  $P(x_0, 0)$  and integrating over  $x_0$  one gets the evolution equation for P(x,t),

$$\frac{\partial}{\partial t}P(x,t) = \hat{\mathcal{L}}(x)P(x,t) . \qquad (2.17)$$

# **III. DETAILED BALANCE**

A consequence of the time reversibility of the microscopic equations of motion in a closed system in equilibrium is the so-called *detailed balance* [14]. When the dynamics of the variable x(t) is described by a master equation like Eq. (2.11), detailed balance is the condition imposing that for each pair of states x and x' the transitions must balance:

$$w(x' \to x)P_e(x') = w(\epsilon x \to \epsilon x')P_e(\epsilon x)$$
 (3.1)

with  $\epsilon = 1$  for even and  $\epsilon = -1$  for odd variables under time reversal. Furthermore, the equilibrium probability distribution satisfies  $P_e(x) = P_e(\epsilon x)$ .

Detailed balance as shown in Eq. (3.1) leads to a similar relationship for the operator  $\hat{\mathcal{W}}(x|x')$  defined in the preceding section [Eq. (2.15)] [3],

$$\hat{\mathcal{W}}(x|x')P_e(x') = \hat{\mathcal{W}}(\epsilon x'|\epsilon x)P_e(x) , \qquad (3.2)$$

which, in turn, leads to the relationship

$$\hat{\mathcal{L}}(x) P_e(x) \psi(x) = P_e(x) \hat{\mathcal{L}}^{\dagger}(\epsilon x) \psi(x) ,$$
 (3.3)

where  $\psi(x)$  is an arbitrary function. The operator  $\hat{\mathcal{L}}^{\dagger}(x)$  is the adjoint of  $\hat{\mathcal{L}}(x)$  in the usual sense and is given by

$$\hat{\mathcal{L}}^{\dagger}(x) \equiv -B(x)\frac{\partial}{\partial x} + \sum_{n=2}^{\infty} \frac{1}{n!} \alpha_n \left(c(x)\frac{\partial}{\partial x}\right)^n$$
. (3.4)

#### **Even variables**

Let us first discuss the case of even variables and thus replace  $\epsilon$  by 1 in Eq. (3.3). Making use now of Eqs. (2.13) and (3.4) in Eq. (3.3) we get

$$\left\{\frac{\partial}{\partial x}B(x) + \sum_{n=2}^{\infty} (-1)^n \frac{1}{n!} \alpha_n \left(\frac{\partial}{\partial x}c(x)\right)^n\right\} P_e(x)\psi(x)$$
$$= P_e(x) \left\{-B(x)\frac{\partial}{\partial x} + \sum_{n=2}^{\infty} \frac{1}{n!} \alpha_n \left(c(x)\frac{\partial}{\partial x}\right)^n\right\} \psi(x) .$$
(3.5)

We now multiply both sides of this last equation by c(x) obtaining

$$\begin{cases} \mathcal{D}B(x) &+ \sum_{n=2}^{\infty} (-1)^n \frac{1}{n!} \alpha_n \mathcal{D}^n c(x) \end{cases} P_e(x) \psi(x) \\ &= P_e(x) \bigg\{ -B(x) \mathcal{D} + \sum_{n=2}^{\infty} \frac{1}{n!} \alpha_n c(x) \mathcal{D}^n \bigg\} \psi(x) \end{cases}$$
(3.6)

where we have introduced the operator  $\mathcal{D}$  as

$$\mathcal{D} \equiv c(x) \frac{\partial}{\partial x} \;.$$
 (3.7)

Expressing the left-hand side of Eq. (3.6) in terms of the independent operators  $\mathcal{D}^n$ , one has

$$\begin{aligned} \left[\mathcal{D}B(x)P_{e}(x)\right]\psi(x) + B(x)P_{e}(x)\mathcal{D}\psi(x) + \sum_{n=2}^{\infty}(-1)^{n}\frac{1}{n!}\alpha_{n}\sum_{m=0}^{n}\binom{n}{m}\left[\mathcal{D}^{n-m}c(x)P_{e}(x)\right]\mathcal{D}^{m}\psi(x) \\ &= P_{e}(x)\left\{-B(x)\mathcal{D} + \sum_{n=2}^{\infty}\frac{1}{n!}\alpha_{n}c(x)\mathcal{D}^{n}\right\}\psi(x) \;. \end{aligned}$$

$$(3.8)$$

Since  $\psi(x)$  is arbitrary, we can now equate the coefficients of the terms proportional to  $\mathcal{D}^m \psi(x)$  in both sides of this last equation. From the coefficient of  $\mathcal{D}^0 \psi(x) = \psi(x)$ , we obtain

$$[\mathcal{D}B(x)P_e(x)] + \sum_{n=2}^{\infty} (-1)^n \frac{1}{n!} \alpha_n \left[ \mathcal{D}^n c(x) P_e(x) \right] = 0 .$$
(3.9)

Dividing this equation by c(x) and using Eq. (3.7), one gets the stationarity condition  $\hat{\mathcal{L}}(x)P_e(x) = 0$  as follows from Eq. (2.17). Similarly, from the coefficient of  $\mathcal{D}\psi(x)$ we get

$$B(x)P_{e}(x) + \sum_{n=2}^{\infty} (-1)^{n} \frac{1}{n!} \alpha_{n} n \left[ \mathcal{D}^{n-1} c(x) P_{e}(x) \right]$$
  
=  $-B(x)P_{e}(x)$  (3.10)

Finally, the coefficient of  $\mathcal{D}^m \psi(x)$  for  $m \geq 2$  gives

$$\sum_{n=m}^{\infty} \frac{1}{n!} (-1)^n \alpha_n \begin{pmatrix} n \\ m \end{pmatrix} \left[ \mathcal{D}^{n-m} c(x) P_e(x) \right]$$
$$= \frac{1}{m!} \alpha_m c(x) P_e(x) \quad \text{for } m \ge 2 .$$
(3.11)

This last expression stands for an homogeneous system of equations for the set of constants  $\alpha_i$  for  $i \geq 2$  whose coefficients are functions of x. Note that  $\alpha_2$  can only appear in the equation for m = 2 in view of the lower limit of the sum on the left-hand side of Eq. (3.11). However, for m = 2 the term containing  $\alpha_2$  in the sum is exactly canceled by the term on the right-hand side, so that  $\alpha_2$  is not determined by this system of equations. In Appendix B we prove that the only acceptable solution of Eqs. (3.11) is  $\alpha_i = 0$  for  $i \geq 3$ . Therefore, L(x,t) in Eq. (2.4) must be Gaussian. This important result was already found in Ref. [11] by using a different procedure.

Thus, Eqs. (3.9) and (3.10) now take, respectively, the form

$$\frac{\partial}{\partial x} \left\{ B(x)P_e(x) + \frac{1}{2}\alpha_2 \left[ c(x)\frac{\partial}{\partial x}c(x)P_e(x) \right] \right\} = 0 ,$$
(3.12)
$$2B(x)P_e(x) + \alpha_2 \left[ c(x)\frac{\partial}{\partial x}c(x)P_e(x) \right] = 0 ,$$
(3.13)

according to the definition of  $\mathcal{D}$ . Notice that Eq. (3.12) can be obtained from Eq. (3.13) by differentiating with respect to x. While the former is the stationarity condition which states that the divergence of the probability flux must be zero in equilibrium, the latter says that the probability flux itself must also vanish.

## **Odd variables**

The treatment of the case of odd variables cannot be carried out following the same procedure as done for even variables for a general nonvanishing c(x). It is, however, of particular importance the situation in which c(x) verifies c(x) = c(-x) since we will prove that L(x,t) is Gaussian *if and only if* c(x) is an even function of its argument. [This was implicitly assumed in Eq. (2.7) of Ref. [11].] Furthermore, we will also determine the corresponding symmetry properties of B(x) and discuss the consequences that arise from these facts.

Let us replace  $\epsilon$  by -1 in Eq. (3.3) and assume that c(x) is even. We then get

$$\begin{cases} \frac{\partial}{\partial x} B(x) + \sum_{n=2}^{\infty} (-1)^n \frac{1}{n!} \alpha_n \left( \frac{\partial}{\partial x} c(x) \right)^n \end{cases} P_e(x) \psi(x) \\ = P_e(x) \left\{ B(-x) \frac{\partial}{\partial x} \right. \\ \left. + \sum_{n=2}^{\infty} (-1)^n \frac{1}{n!} \alpha_n \left( c(x) \frac{\partial}{\partial x} \right)^n \right\} \psi(x) . \qquad (3.14) \end{cases}$$

Using again the operator  $\mathcal{D}$  and equating the coefficients of the functions  $\mathcal{D}^m \psi(x)$  at both sides of Eq. (3.14), we arrive at

$$[\mathcal{D}B(x)P_e(x)] + \sum_{n=2}^{\infty} (-1)^n \frac{1}{n!} \alpha_n \left[\mathcal{D}^n c(x)P_e(x)\right] = 0$$
(3.15)

for the coefficient of  $\mathcal{D}^0\psi(x)$ . From the term proportional to  $\mathcal{D}\psi(x)$  we get

$$B(x)P_e(x) + \sum_{n=2}^{\infty} (-1)^n \frac{1}{n!} \alpha_n n \left[ \mathcal{D}^{n-1} c(x) P_e(x) \right]$$
  
=  $B(-x)P_e(x)$ . (3.16)

The coefficient of  $\mathcal{D}^m \psi(x)$  for  $m \geq 2$  gives

$$\sum_{n=m}^{\infty} \frac{1}{n!} (-1)^n \alpha_n \begin{pmatrix} n \\ m \end{pmatrix} \left[ \mathcal{D}^{n-m} c(x) P_e(x) \right]$$
$$= (-1)^m \frac{1}{m!} \alpha_m c(x) P_e(x) \quad \text{for } m \ge 2 .$$
(3.17)

In Appendix B we also prove that the only acceptable solution of this last equation is  $\alpha_i = 0$  for  $i \ge 3$ , so that L(x,t) is again a Gaussian process.

The reverse implication is not difficult to prove. Let us assume that L(x,t) is a Gaussian process or, what is the same, that  $\alpha_i = 0$  for  $i \geq 3$ . From Eq. (3.3) with  $\epsilon = -1$ , making use of Eqs. (2.13) and (3.4) we obtain

$$\begin{cases} \frac{\partial}{\partial x} B(x) + \frac{1}{2} \alpha_2 \left( \frac{\partial}{\partial x} c(x) \right)^2 \end{cases} P_e(x) \psi(x) \\ = P_e(x) \left\{ B(-x) \frac{\partial}{\partial x} + \frac{1}{2} \alpha_2 \left( c(-x) \frac{\partial}{\partial x} \right)^2 \right\} \psi(x) , \end{cases}$$
(3.18)

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where now c(x) is a general nonvanishing function. Equating the coefficients of the terms proportional to  $\partial^2 \psi(x)/\partial x^2$ , we get

$$\frac{1}{2}\alpha_2 c^2(x) P_e(x) = \frac{1}{2}\alpha_2 c^2(-x) P_e(x)$$
(3.19)

and since c(x) is assumed nonvanishing, then c(x) = c(-x). Therefore, if detailed balance is satisfied and x(t) is an odd variable under time reversal, L(x, t) is Gaussian if and only if c(x) is an even function.

Making use of the Gaussian nature of L(x,t), Eqs. (3.15) and (3.16) become

$$\frac{\partial}{\partial x} \left\{ B(x)P_e(x) + \frac{1}{2}\alpha_2 \left[ c(x)\frac{\partial}{\partial x}c(x)P_e(x) \right] \right\} = 0 ,$$
(3.20)
$$[B(x) - B(-x)]P_e(x) + \alpha_2 \left[ c(x)\frac{\partial}{\partial x}c(x)P_e(x) \right] = 0 .$$
(3.21)

Again, Eq. (3.20) has the structure of the divergence of a flux equal to zero. Since this flux itself is zero in equilibrium, we get

$$B(x) = -B(-x)$$
. (3.22)

Thus, under these conditions Eqs. (3.20) and (3.21) reduce to Eqs. (3.12) and (3.13) and, therefore, under these circumstances the subsequent discussion will be valid for even as well as for odd variables.

While Eq. (3.22) follows from detailed balance, we will prove in the next section that if weak coupling is satisfied, this previous symmetry implies in turn

$$\Gamma(x) = -\Gamma(-x) , \qquad (3.23)$$

$$\beta(x) = \beta(-x) . \tag{3.24}$$

#### The Fokker-Planck equation

Let us consider again Eq. (3.13). In view of Eq. (2.2) it can be written as

$$\left(\frac{\alpha_2}{2}c^2(x) - \beta(x)\right)\frac{d}{dx}\ln P_e(x) = \Gamma(x) - \frac{1}{2}\frac{d}{dx}\frac{\alpha_2}{2}c^2(x) .$$
(3.25)

Note that the factor  $\alpha_2/2$  may be absorbed into  $c^2(x)$ . In what follows, we will, without loss of generality, choose the scale of L(x,t) such that  $\alpha_2 = 2$ . Then, Eq. (3.25) turns into

$$[c^{2}(x) - \beta(x)] rac{d}{dx} \ln P_{e}(x) = \Gamma(x) - rac{1}{2} rac{d}{dx} c^{2}(x)$$
. (3.26)

With the aim of discussing the original Langevin Eq. (1.12) or, equivalently, Eq. (2.5), we have to relate the previous results with those corresponding to Îto's prescription. It is easy to show [3], although we will not do it here, that for  $\tilde{\Gamma}(x)$ ,  $\tilde{c}(x)$ , and  $\tilde{L}(x,t)$ , one can find that (i)  $\tilde{L}(x,t)$  is also Gaussian with  $\tilde{c}_2(x,x') = \tilde{c}(x)\tilde{c}(x')$ , (ii)

 $\tilde{\Gamma}(x)$  and  $\tilde{c}(x)$  are related by the equation

$$\left[\tilde{c}^2(x) - \beta(x)\right] \frac{d}{dx} \ln P_e(x) = \tilde{\Gamma}(x) - \frac{d}{dx} \tilde{c}^2(x) , \quad (3.27)$$

and, for odd variables, (iii) the same symmetries as in Eqs. (3.22)-(3.24) hold.

Equation (3.28), bearing two unknown functions  $\overline{\Gamma}(x)$ and  $\tilde{c}(x)$ , indicates that for our Langevin equation, microscopic reversibility alone cannot unequivocally determine the properties of the random force  $\tilde{F}(x(t),t)$ . Rather, it relates the functions  $\overline{\Gamma}(x)$  and  $\tilde{c}(x)$  with the thermodynamic force and the phenomenological coefficient  $\beta(x)$ . In the next section we will introduce a plausible way to determine these two functions based on physical grounds.

Equation (3.27), the fact that the random process  $\tilde{L}(x,t)$  must be Gaussian as well as the symmetries of  $\tilde{\Gamma}(x)$ ,  $\tilde{c}(x)$ , and  $\beta(x)$  for odd variables, constitute the main results of this section. Some consequences follow.

First, in view of the fact that  $\tilde{L}(x,t)$  must be a Gaussian process, then Eq. (1.12) is equivalent to a Fokker-Planck equation of the form

$$\frac{\partial}{\partial t}P(x,t) = \frac{\partial}{\partial x} \left( \tilde{B}(x) P(x,t) + \frac{\partial}{\partial x} \tilde{c}^2(x) P(x,t) \right) .$$
(3.28)

Second, integrating Eq. (3.27) we get

$$\begin{split} \tilde{c}^2(x) &= \frac{\Omega}{P_e(x)} + \beta(x) \\ &- \frac{1}{P_e(x)} \int dx' \, P_e(x') \left\{ \frac{d}{dx'} \beta(x') - \tilde{\Gamma}(x') \right\} \\ &\equiv \beta(x) - \Lambda(x) \;, \end{split}$$
(3.29)

where  $\Omega$  is an integration constant. In this last expression we have gathered in  $\Lambda(x)$  all the terms that explicitly depend on the equilibrium probability distribution  $P_e(x)$ . Note that, in general, the properties of the random force are then dependent on the Onsager coefficient  $\beta(x)$  as well as on the equilibrium probability distribution.

Inserting this last expression for  $\tilde{c}^2(x)$  into Eq. (3.28), after some algebra, one gets

$$\frac{\partial}{\partial t}P(x,t) = \frac{\partial}{\partial x}\left[\beta(x) - \Lambda(x)\right] \left[-P(x,t)\frac{\partial}{\partial x}\ln P_e(x) + \frac{\partial}{\partial x}P(x,t)\right] .$$
(3.30)

Note that this equation depends on the still unknown function  $\tilde{\Gamma}(x)$  in view of Eq. (3.29). Nevertheless, independently of that function, the equilibrium probability distribution  $P_e(x)$  is always a solution of this equation.

Finally, after remark 2 and due to the fact that  $\Gamma(x)$  is not necessarily zero for a linear A(x), we have no objective reason at this point to consider the theory for linear A(x) as substantially different from that of the genuinely nonlinear case.

## **IV. TWO EXAMPLES**

In this section we will analyze two nontrivial examples for which a more detailed analysis exists. The first one is the diffusion of a Brownian particle with a positiondependent friction coefficient in a general potential field. The second one is a diode with a nonsymmetric nonlinear characteristic function I = I(V).

## **Diffusion of Brownian particles**

Here, we will study the case in which the variable x(t) is the position of a Brownian particle in a onedimensional system in equilibrium with a reservoir that keeps constant the temperature T. The particle is sensitive to a potential field V(x). Thus, the equilibrium distribution function is given by

$$P_e(x) = \frac{1}{N} e^{-V(x)/kT}$$
, (4.1)

where  $\mathcal{N}$  is the normalization constant and k is Boltzmann's constant. The phenomenological equation in this case is the relationship between the velocity of the particle and the force acting on it,

$$\dot{X}(t) = -\frac{1}{\xi(X)} \frac{d}{dX} V(X) \equiv -A(X) , \qquad (4.2)$$

 $\xi(X)$  being the friction coefficient which is assumed to be position-dependent. Physical examples could be either motion in an inhomogeneous medium, or an analogy with the three-dimensional situation where hydrodynamic interactions with other particles or with the walls of the container cause the friction coefficient of a Brownian particle to change from one point to another. From these two equations we can rewrite A(X) as

$$A(X) = \frac{1}{\xi(X)} \frac{d}{dX} V(X) = -\frac{kT}{\xi(X)} \frac{d}{dX} \ln P_e(X) \quad (4.3)$$

which permits us to identify  $\beta(X) = kT/\xi(X)$ . To describe the fluctuations, let us replace X by x and rewrite an equation of the form of Eq. (2.1),

$$\dot{x}(t) = \left[\frac{kT}{\xi(x(t))}\frac{d}{dx}\ln P_e(x) + \tilde{\Gamma}(x(t))\right] + \tilde{F}(x(t),t) ,$$
(4.4)

where the term between brackets is  $\hat{B}(x(t))$ . If detailed balance has to be satisfied, the corresponding Fokker-Planck equation then reads

$$\frac{\partial}{\partial t}P(x,t) = \frac{\partial}{\partial x} \left(\frac{kT}{\xi(x)} - \Lambda(x)\right) \left[P(x,t) \frac{\partial}{\partial x} \frac{V(x)}{kT} + \frac{\partial}{\partial x}P(x,t)\right] .$$
(4.5)

Note that this equation does not coincide with the wellknown Smoluchowski equation that describes the diffusion of Brownian particles with position-dependent friction coefficient (see, for instance, Refs. [3,15]) unless  $\Lambda(x)$  identically vanishes.

At this point we will further assume that the properties of the random force need to be independent of  $P_e(x)$ . (This statement will be referred to as "weak coupling" from now on.) If this is the case, from Eq. (3.27) we get that, in general,

$$\tilde{c}^2(x) = \beta(x) , \qquad (4.6)$$

$$\tilde{\Gamma}(x) = rac{d}{dx} eta(x) , \qquad (4.7)$$

so that the random force is completely characterized. To get a more intuitive picture of the physical nature of this statement, in the case of Brownian motion, we may say that weak coupling is equivalent to state that the random force should be a property of the bath system and then it must be independent of the potential force, -dV(x)/dx, externally applied to the Brownian particle. Then, if Eq. (4.7) is satisfied,  $\Lambda(x)$  identically vanishes and the usual diffusion equation is recovered.

Note that in the case of odd variables, since we have assumed that  $\tilde{c}(x)$  is even, Eqs. (4.6) and (4.7) lead to the symmetry properties shown in Eqs. (3.23) and (3.24).

We can then conclude that our Langevin equation (1.12) is completely determined when detailed balance and weak coupling are imposed, leading us to the Gaussian nature of L(x,t) and to Eqs. (4.6) and (4.7). We have also found that such a Langevin equation is equivalent to the Fokker-Planck equation

$$\frac{\partial}{\partial t}P(x,t) = \frac{\partial}{\partial x}\beta(x)\left[P(x,t)\left(-\frac{\partial}{\partial x}\ln P_e(x)\right) + \frac{\partial}{\partial x}P(x,t)\right]$$
(4.8)

for the probability distribution.

### Diode

We will next consider the problem proposed in Refs. [12,13], where an extensive analysis on more microscopic grounds can be found. One is now interested in the study of charge fluctuations in a condenser of capacity C in parallel with a vacuum diode which is in thermal equilibrium with a reservoir at a temperature T. The diode is constructed by facing two electrodes of metals with different work functions (the work functions are defined as the work needed to extract an electron from the metal) for the electrons,  $W_1$  and  $W_2$  with  $W_1 > W_2$ . The system is described in the scheme of Fig. 1. It is important to note that we have explicitly included in the figure the contact potential barrier, equal to the difference in electrochemical potential per unit charge, when one electron passes from one metal to the other. This contact potential is  $\Delta W/e$ , where  $\Delta W = W_1 - W_2$  and e is the electron's elementary charge. For the system of the figure we have the I(V) characteristics

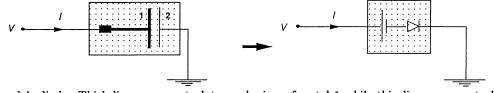


FIG. 1. Alkemade's diode. Thick lines represent plates and wires of metal 1 while thin lines represent plates and wires of metal 2. The system enclosed by the frame corresponds to the diode and it is kept at constant temperature T. The figure on the right-hand side represents a schematic view of the system. Note that the junction of metals 1 and 2 give rise to a potential barrier.

$$I(V) = I_0 \left( e^{eV/kT} - 1 \right) .$$
 (4.9)

The relation between the intensity and the voltage difference v between the diode plates is obtained by using in Eq. (4.9) the fact that  $V = \Delta W/e + v$  as it follows from the figure. It then reads

$$I(v) = I_0 \left( e^{\Delta W/kT} e^{ev/kT} - 1 \right) .$$
 (4.10)

One way to proceed is to connect a condenser of capacity C in parallel with the system of Fig. 1 to study charge fluctuations in the condenser originated in the diode. In that case, the equilibrium distribution for the charge in the condenser follows by standard equilibrium statistical mechanics. Effectively, the energy of the condenser when storing a charge q is purely electrostatic and equal to  $E = q^2/2C$ . Then, the equilibrium distribution is given by

$$P_e(q) \sim e^{-\frac{q^2}{2kTC}}$$
 . (4.11)

With the equilibrium distribution (4.11) and the phenomenological law (4.9), one can obtain the equation for the fluctuations following the same procedure as in the previous example. The system studied in Refs. [12,13] is, however, slightly different and corresponds to that shown in Fig. 2. Note that since the system has no contacts, the plates of the condenser need to be of different metals. This crucial point leads us to the equilibrium distribution function for the charge in the condenser. One considers again the energy of the condenser when a charge q is stored. To discharge the condenser, on one hand, the electrons lose electrostatic energy in traveling from metal 2 (where the voltage is 0 according to Fig. 2) to metal 1 (where the voltage is v = q/C). On the other hand, there is an additional loss of energy due to the fact that the chemical potential of the electrons in metal 2 is higher (lower work function) than in metal 1 (higher work function). The energy stored in the condenser is thus  $E = q^2/2C + \Delta W q/e$  and the equilibrium distribution reads

$$P_e(q) \sim e^{-\frac{q^2}{2kTC} - \frac{\Delta Wq}{KTe}} . \qquad (4.12)$$

The equilibrium charge  $q_0$  of the condenser is thus

$$q_0 = -\frac{\Delta W C}{e} \ . \tag{4.13}$$

These results obtained using equilibrium statistical mechanics are also found in Ref. [13] from the master equation proposed to describe the system under discussion. Moreover, the fact that the condenser in equilibrium bears a charge  $q_0$  could be interpreted as a violation of the second law of thermodynamics. It is clear from the fact that the two plates of the condenser are of different metals that, in equilibrium, no work can be obtained by connecting them with a wire since the equilibrium voltage  $v_0 \equiv q_0/C = -\Delta W/e$  would exactly be compensated by a contact voltage barrier due to the difference in electrochemical potentials.

Consequently, in order to study charge fluctuations in this system, we have to use Eq. (4.12) together with Eq. (4.10). In view of Fig. 2, note that the charge in the condenser decreases when I is positive. Thus, the phenomenological equation for this system is obtained from Eq. (4.10) and reads

$$\dot{q} = -I(v) = I_0 \left( 1 - e^{e(q-q_0)/kTC} \right) ,$$
 (4.14)

where Eq. (4.13) has been used. Finally, with the aim of comparing with the results obtained in Ref. [13], we rewrite Eqs. (4.12) and (4.14) in terms of the dimensionless variable  $x \equiv -\epsilon^{1/2}(q-q_0)/e$ , where  $\epsilon \equiv e^2/kTC$  is a small parameter that is related to the amplitude of the fluctuations. (This parameter is related to the inverse of the size of the system, in this case the capacity of the condenser C [3]. Physically,  $\epsilon$  measures the ratio between the difference in electrostatic energy between two consecutive electron jumps and kT. The jump probability of a second electron is strongly affected by the jump of the first one if  $\epsilon \sim 1$ .) We get

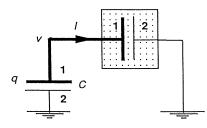


FIG. 2. Alkemade's diode in parallel with a condenser. To avoid the junction in the wires, the plates of the condenser are of different metals. We study the charge fluctuations q in the condenser of capacity C.

$$P_e(x) \sim e^{-x^2/2}$$
 (4.15)

and

$$\dot{x} = j \left( e^{-\epsilon^{1/2} x} - 1 \right) ,$$
 (4.16)

where  $j \equiv I_0 \epsilon^{1/2}/e$ . As in the previous example, from these two equations we obtain the phenomenological coefficient  $\beta(x)$ ,

$$\beta(x) = \frac{j}{x} \left( 1 - e^{-\epsilon^{1/2}x} \right) .$$
 (4.17)

Finally, making use of Eqs. (4.15) and (4.17) in Eq. (4.8) we arrive at

$$\frac{\partial}{\partial t}P(x,t) = \frac{\partial}{\partial x}\frac{j}{x}\left(1 - e^{-\epsilon^{1/2}x}\right)\left[xP(x,t) + \frac{\partial}{\partial x}P(x,t)\right].$$
(4.18)

To end this section, we compare Eq. (4.18) with the expansion of the master equation for this model. We thus expand our Fokker-Planck equation in powers of  $\epsilon^{1/2}$ . We obtain

$$\frac{1}{j\epsilon^{1/2}}\frac{\partial}{\partial t}P(x,t) = \frac{\partial}{\partial x}[x - \frac{1}{2}\epsilon^{1/2}(x^2 - 1) + \frac{1}{6}\epsilon(x^3 - 2x)]P(x,t) + \frac{\partial^2}{\partial x^2}(1 - \frac{1}{2}\epsilon^{1/2}x + \frac{1}{6}\epsilon x^2)P(x,t) + O(\epsilon^{3/2}). \quad (4.19)$$

On the other hand, Eq. (45) of Ref. [13] has the form

$$\frac{\partial}{\partial \tau} P(x,t) = \frac{\partial}{\partial x} [x - \frac{1}{2} \epsilon^{1/2} (x^2 - 1) + \frac{1}{6} \epsilon (x^3 - 3x)] P(x,t) + \frac{\partial^2}{\partial x^2} [1 - \frac{1}{2} \epsilon^{1/2} x + \frac{1}{4} \epsilon (x^2 - 1)] P(x,t) + \frac{\partial^3}{\partial x^3} (\frac{1}{6} \epsilon x) P(x,t) + \frac{1}{12} \epsilon \frac{\partial^4}{\partial x^4} P(x,t) + O(\epsilon^{3/2}) .$$
(4.20)

Comparing these last two equations we see that they agree up to order  $\epsilon^{1/2}$ , while up to first order the equation for the fluctuations is not even a Fokker-Planck equation but higher order derivatives have appeared. We then conclude first that to the order of validity of the Fokker-Planck equation itself,  $(\epsilon^{1/2})$ , the fluctuations are correctly described by the phenomenological theory developed in this paper without ambiguity. Second, up to this order, the coefficients of the Fokker-Planck equation are functions of the variable x, corresponding to a so-called nonlinear Fokker-Planck equation. The possibility of correctly set nonlinear Fokker-Planck equations from a phenomenological theory is the main result of this paper. As we have seen, however, the validity of the Fokker-Planck equation to describe fluctuations in nonlinear systems is restricted to small fluctuations.

#### **V. CONCLUSIONS**

In this paper we have tried to answer the question of whether it is possible or not to write a Langevin equation to describe the equilibrium fluctuations of a given macroscopic variable X with only a phenomenological knowledge of the system. To this end, we have proposed the Langevin equation (1.12) containing two terms accounting for the existence of fluctuations. In the first place, we have a function  $\Gamma(x)$  which plays the role of a modification of the phenomenological law at the scale of the fluctuations. This answers one of the major criticisms of the use of Langevin equation to describe fluctuations in nonlinear systems [3]. In the second place, we have introduced a causal random force as given in Eq. (1.8). We have then analyzed the particular case in which the cumulants of  $\tilde{L}(x,t)$  depend on a single function  $\tilde{c}(x)$ , which is equivalent to a multiplicative noise, which is the

simplest case of variable-dependent random force. Then, the function  $\tilde{c}(x)$  can be interpreted as an amplitude of the random force that can vary from point to point. We have proved that detailed balance leads, first, to the result that  $\hat{L}(x,t)$  must be a Gaussian process. One important consequence of this result is that our Langevin equation (1.12) is equivalent to a Fokker-Planck equation. Second, we have obtained the relationship between the functions  $\Gamma(x)$  and  $\tilde{c}(x)$  given in Eq. (3.27). While these are general results for even variables, we have seen that they are only satisfied for odd variables under certain symmetry conditions. In fact, in this last situation we have proved that  $\tilde{L}(x,t)$  is a Gaussian process if and only if  $\tilde{c}(x)$  is an even function, which also implies that  $\tilde{B}(x)$  must be odd. The symmetry of this "renormalized" flux leads in turn to the fact that  $\tilde{\Gamma}(x)$  has to be odd and the Onsager coefficient  $\beta(x)$  has to be an even function. This is an important condition on the phenomenological coefficient that arises from microscopic reversibility and weak coupling, which has the same origin as the symmetry of the Onsager coefficients for the crossed terms in the linear case [6].

Moreover, we have seen that the phenomenological knowledge of the system together with detailed balance are not enough to determine the properties of the random force. The existence of this ambiguity indicates that, at this level, different equations for the fluctuations could be proposed, all satisfying detailed balance and having the same equilibrium probability distribution, but leading to different dynamics for the fluctuations [13]. We have then shown that, if the internal mechanism that causes the random force is weakly coupled with the variable that fluctuates, as it has clearly been shown in the case of Brownian motion, detailed balance together with this weak coupling assumption suffices to completely determine the Langevin equation. In our analysis we have imposed weak coupling only at a later stage of the discussion in order to completely specify the properties of the random force, after having applied detailed balance. It is important to note, however, that if we had imposed detailed balance together with weak coupling from the beginning, we would have seen that the Gaussian nature of L(x,t) follows both for variables even and odd under time-reversal, that the "renormalized" flux is automatically acceptable, and that the symmetry property of  $\beta(x)$  is a natural consequence of both principles. [This can be proved by treating in Eq. (3.3) both  $\psi(x)$  and  $P_e(x)$  as arbitrary functions and following the same reasoning as in Appendix B but for a general c(x).]

The results derived from the previous analysis have been applied to two nontrivial examples. To the range of validity of the form assumed for the random force in Eq. (1.8), the results coincide with more detailed models for the dynamics of the fluctuations in those systems. Taking into account that for a general process the validity of the Fokker-Planck equation as an approximation of the master equation is restricted to small fluctuations [3], in the second example of Sec. IV we have seen that, to the range of validity of the Fokker-Planck equation itself, our approach is correct and furnishes a description of the fluctuations in a genuinely nonlinear system. Therefore, all the results found here by means of a phenomenological analysis are consistent with those obtained from the expansion of the master equation.

Let us analyze the case  $\beta$  constant in more detail. From Eqs. (4.6) and (4.7), we get that  $\tilde{c}^2 = \beta$  (also constant) and  $\tilde{\Gamma} = 0$ , in agreement with Ref. [9] which, for linear Langevin equations, reduces to the standard results. It is important to realize that detailed balance alone ensures, in view of Eq. (3.27), that  $\langle \tilde{\Gamma}(x) \rangle = 0$ , but still  $\tilde{\Gamma}(x)$  and  $\tilde{c}(x)$  can be nonconstant functions related by Eq. (3.27). Therefore, the standard theory for Langevin equations, either linear or with constant  $\beta$ , relies on an implicit weak coupling assumption. [This implicit weak coupling assumption is formulated by demanding that the random force F(x(t), t) is independent of the variable x(t).]

On the basis of causality and stationarity, the second moment of the random force in a nonlinear Langevin equation of the type (2.1), has been proved to satisfy [10]

$$\langle F(x(t),t)F(x(t'),t')\rangle = \langle \tilde{L}(x(t),t)\tilde{L}(x(t'),t')\rangle$$
  
= 2\langle x(t)\tilde{B}(x(t))\rangle \delta(t-t'). (5.1)

Inserting the definition of  $\tilde{B}(x)$  in the right-hand side of this equation, after partial integration we get

$$\langle x(t)\tilde{B}(x(t))\rangle = \langle \beta(x(t))\rangle + \left\langle x(t) \left. \frac{d}{dx} \beta(x) \right|_{x=x(t)} \right\rangle$$
  
  $-\langle x(t)\tilde{\Gamma}(x(t))\rangle .$  (5.2)

If detailed balance applies, one can make use of Eq. (4.7). Then, the second and third terms in this last equation cancel and we finally obtain [16]

$$\langle F(x(t),t)F(x(t'),t')\rangle = 2\langle \beta(x(t))\rangle \,\delta(t-t') \,.$$
 (5.3)

Again, if  $\beta$  is constant, only now we recover the fluctuation-dissipation theorem as a consequence of both detailed balance and weak coupling. In the genuinely nonlinear case, Eq. (5.3) as well as Eq. (4.6) are reminiscent of the fluctuation-dissipation theorem existing for linear systems. In particular, Eq. (4.6) relates the amplitude of the random force,  $\tilde{c}(x)$ , to the phenomenological coefficient  $\beta(x)$  at every point.

Finally, one can calculate the average of the flux in equilibrium from Eq. (1.12). Effectively, from causality and Eq. (3.27) it follows that

$$\langle \dot{x}(t) \rangle = \left\langle \beta(x(t)) \frac{d}{dx} \ln P_e(x) \right|_{x=x(t)}$$

$$+ \frac{d}{dx} \beta(x) \Big|_{x=x(t)} \right\rangle \equiv 0$$
(5.4)

as expected. Notice that the underlined term is the modification of the phenomenological law due to the fluctuations and ensures that  $\langle \dot{x} \rangle$  is zero in equilibrium, so that there is no violation of the second law as is the case in the so-called "Brillouin paradox" [3].

### ACKNOWLEDGMENTS

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## APPENDIX A: DERIVATION OF THE MASTER EQUATION

The density distribution given in Eq. (2.7) satisfies a continuity equation

$$rac{\partial}{\partial t}
ho(x,t) = -rac{\partial}{\partial x}\dot{x}(x,t)\,
ho(x,t).$$
 (A1)

In view of Eq. (2.7), and due to the properties of the  $\delta$ -function, to compute  $\dot{x}(x,t)$  we can use Eq. (2.4) replacing the random variable x(t) by the field variable x, giving

$$rac{\partial}{\partial t}
ho(x,t) = -rac{\partial}{\partial x}\left[-B(x) + L(x,t)
ight]
ho(x,t)$$
 (A2)

where use has been made of Eq. (1.8). Equation (A2) can be formally solved, obtaining

$$\rho(x,t) = \left\{ \exp \int_0^t dt' \, \frac{\partial}{\partial x} \left[ B(x) - L(x,t) \right] \right\} \delta(x - x_0) \,, \tag{A3}$$

where use has been made of  $\rho(x, t = 0) = \delta(x - x_0)$ . Note that the term between curly brackets is independent of the initial condition  $x_0$  since x is not a random variable but a field point and the process L(x,t) has been assumed to be independent of x(t), so that it is also independent of  $x(t = 0) = x_0$ . Thus, we can average both members of this last equation and use Eq. (2.8) to also derive the formal solution for the conditional probability density

$$P(x,t|x_0) = \left\langle \exp \int_0^t dt' \, \frac{\partial}{\partial x} \left[ B(x) - L(x,t) \right] \right\rangle P(x,t=0|x_0) \,. \tag{A4}$$

The average is performed over all the realizations of L(x,t) and it is independent of  $x_0$ . This last expression can also be written in terms of the cumulants

$$P(x,t|x_0) = \exp\left\{\sum_{n=1}^{\infty} \frac{1}{n!} \left\langle \left(\int_0^t dt' \frac{\partial}{\partial x} \left[B(x) - L(x,t)\right]\right)^n \right\rangle_c \right\} P(x,t=0|x_0) .$$
(A5)

For n = 1 one has

$$\left\langle \left( \int_0^t dt' \frac{\partial}{\partial x} \left[ B(x) - L(x,t) \right] \right) \right\rangle_c$$
$$= \int_0^t dt' \frac{\partial}{\partial x} \left[ B(x) - \langle L(x,t) \rangle_c \right] = t \frac{\partial}{\partial x} B(x) . \quad (A6)$$

For  $n \geq 2$  one has

$$\left\langle \left( \int_0^t dt' \, \frac{\partial}{\partial x} \left[ B(x) - L(x,t) \right] \right)^n \right\rangle_c$$
$$= (-1)^n t \, \alpha_n \left( \frac{\partial}{\partial x} c(x) \right)^n , \qquad (A7)$$

where in deriving the last line use has been made of Eqs. (1.11) and (2.6). Therefore, substituting these results into Eq. (A5) one gets

$$P(x,t|x_0) = \exp\left\{t\left[\frac{\partial}{\partial x}B(x) + \sum_{n=2}^{\infty} (-1)^n \frac{1}{n!}\alpha_n \left(\frac{\partial}{\partial x}c(x)\right)^n\right]\right\}$$
$$\times P(x,t=0|x_0). \tag{A8}$$

Differentiating with respect to time, one arrives at Eq. (2.10).

# APPENDIX B: PROOF OF $\alpha_I = 0$ FOR $I \ge 3$

In this appendix we will show the possible solutions of the system of Eqs. (3.11) and (3.17) for the parameters  $\alpha_i$ ,  $i \geq 2$ . Once removed  $\alpha_2$  (recall that the coefficient of the only term involving this constant is zero), the system is a homogeneous set of equations for  $\alpha_i$  for  $i \geq 3$  with *x*-dependent coefficients. Its solution is  $\alpha_i = 0$  for  $i \geq 3$ if the determinant is nonzero and, therefore, L(x,t) is a Gaussian process. However, if its determinant is zero, then other solutions with some  $\alpha_i \neq 0$  may exist. In order to find the expression of the determinant, let us separately write the equations for *m* even and odd. From (3.11) and (3.17) it follows that

$$-\frac{1}{(2k)!}\mathcal{D}y(x)\alpha_{2k+1} + \sum_{n=2k+2}^{\infty} \frac{1}{n!} \binom{n}{2k} \mathcal{D}^{n-2k}y(x)\alpha_n = 0, \quad m = 2k ,$$
(B1)

$$-\frac{1+\epsilon}{(2k+1)!}y(x)\alpha_{2k+1} + \sum_{n=2k+2}^{\infty}\frac{1}{n!}\binom{n}{2k+1}\mathcal{D}^{n-(2k+1)}y(x)\alpha_n = 0, \quad m = 2k+1 ,$$
(B2)

with k = 1, 2, .... We have defined the function  $y(x) \equiv c(x)P_e(x)$  for ease of notation.

Let us first consider the case of even variables. We thus replace  $\epsilon$  by 1 in Eq. (B2). Making use of this last equation, we can express the coefficient of  $\alpha_{2k+1}$  in terms of all higher ones. If one then proceeds to substitute Eq. (B2) systematically for all k in Eq. (B1), one arrives at a set of equations only for the even coefficients. Moreover, this new set of equations is triangular and it is then sufficient to calculate the terms of the diagonal in order to know its determinant. One can see that the determinant is zero only if

$$y(x)[-(\mathcal{D}y(x))^2 + y(x)\mathcal{D}^2y(x)] = 0$$
 (B3)

which implies that some  $\alpha_i$  may be nonzero if y(x) satisfies the nonlinear differential equation

$$-c^2(x)\left(rac{dy}{dx}
ight)^2+c(x)y(x)rac{dc}{dx}rac{dy}{dx}+c^2(x)y(x)rac{d^2y}{dx^2}=0 \;,$$
(B4)

whose solutions are

$$y(x) = c(x)P_e(x) = \nu + \mu \int P_e(x)dx$$
, (B5)

 $\nu$  and  $\mu$  being integration constants. This last equation determines c(x), since  $P_e(x)$  has been considered as given. Note that in this particular case, c(x) is independent of the phenomenological coefficient  $\beta(x)$ . Furthermore, these solutions are eigenfunctions of the differential operator  $\mathcal{D}$ ,

$$\mathcal{D}y(x) = \mu y(x)$$
 . (B6)

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In order to determine the set of cumulants  $\alpha_i$ , we will use this last property in Eqs. (3.9) and (3.10). We get

$$\frac{\mathcal{D}B(x)P_e(x)}{y(x)} = -\sum_{n=2}^{\infty} \frac{(-1)^n}{n!} \mu^n \alpha_n , \qquad (B7)$$

$$\frac{2B(x)P_e(x)}{y(x)} = -\sum_{n=2}^{\infty} \frac{(-1)^n n}{n!} \mu^{n-1} \alpha_n .$$
 (B8)

Let us introduce the function

$$\psi(\mu) = \sum_{n=2}^{\infty} \frac{(-1)^n}{n!} \mu^n \alpha_n \tag{B9}$$

in terms of which Eqs. (B7) and (B8) become

$$\frac{\mathcal{D}B(x)P_e(x)}{y(x)} = -\psi(\mu) , \qquad (B10)$$

$$\frac{2B(x)P_e(x)}{y(x)} = -\frac{\partial\psi(\mu)}{\partial\mu} . \tag{B11}$$

Thus, eliminating B(x) between Eqs. (B10) and (B11), we obtain a differential equation for  $\psi(\mu)$ ,

$$\frac{d\psi}{d\mu} - \frac{2\psi}{\mu} = 0 , \qquad (B12)$$

which indicates that  $\psi$  is a quadratic function of the parameter  $\mu$ . This implies that all the cumulants of L(x,t) should be zero except for the second one. Therefore, we have proved that also in this case L(x,t) is Gaussian. Moreover, from Eqs. (B9)–(B11) we arrive at the corre-

- [1] P. Langevin, C. R. Acad. Sci. (Paris) 146, 530 (1908).
- [2] G.E. Uhlenbeck and L.S. Ornstein, Phys. Rev. 34, 823 (1930), reprinted in N. Wax, Selected Papers on Noise and Stochastic Process (Dover, New York, 1954).
- [3] N.G. van Kampen, Stochastic Processes in Physics and Chemistry, 2nd ed. (North Holland, Amsterdam, 1992).
- [4] L. Landau and E.M. Lifshitz, Fluid Mechanics (Pergamon, New York, 1959).
- [5] L. Onsager and S. Machlup, Phys. Rev. 36, 823 (1953).
- [6] S.R. de Groot and P. Mazur, Non-equilibrium Thermodynamics (Dover, New York, 1984).
- [7] See Ref. [3], Chap. IX, Secs. 4-5; in particular pp. 228 and 234-237.
- [8] See Ref. [3], p. 235.

sponding Langevin equation

$$\frac{dx}{dt} = \frac{c(x)}{2}\alpha_2\mu + L(x,t) .$$
 (B13)

Now, in view of Eq. (B5), we see that Eq. (B13) is independent of the phenomenological coefficient  $\beta(x)$ , corresponding to a situation which is out of the scope of this work.

Let us finally point out that the special case  $\mu = 0$  leads to a Langevin equation of the form

$$\frac{dx}{dt} = L(x,t) , \qquad (B14)$$

which is again nonacceptable. In this case, however, detailed balance does no state to completely fix the properties of L(x,t). Although all the odd cumulants are zero, the even ones remain undetermined, allowing therefore for non-Gaussian noises.

For odd variables, we have to replace  $\epsilon$  by -1 in Eqs. (B1) and (B2). In this case, the first term in Eq. (B2) vanishes. Therefore, the homogeneous system of equations is already triangular, showing that  $\alpha_i = 0$  for  $i \geq 3$ , unless the determinant is zero. This happens only if

$$\mathcal{D}y = 0 . \tag{B15}$$

In this case, nothing can be said about the set of cumulants  $\alpha_i$ , since in view of Eq. (B15), in Eqs. (B1) and (B2) all the coefficients vanish. The corresponding Langevin equation also has the form given in Eq. (B14), again nonacceptable.

- [9] P. Mazur and D. Bedeaux, Physica A 173, 155 (1991); P. Mazur and D. Bedeaux, Biophys. Chem. 41, 41 (1991).
- [10] P. Mazur, Phys. Rev. A 45, 8957 (1992).
- [11] P. Mazur and D. Bedeaux, Langmuir 8, 2947 (1992).
- [12] C.T.J. Alkemade, Physica 24, 1029 (1958).
- [13] N.G. van Kampen, in Fluctuation Phenomena in Solids, edited by R.E. Burgess (Academic Press, New York, 1965), Chap. 5.
- [14] See Ref. [6], pp. 98–99.; see also Ref. [3], Chap. V, Secs.4 and 6 and references therein.
- [15] J.M. Sancho, M. San Miguel, and D. Dürr, J. Stat. Phys. 28, 291 (1982).
- [16] P. Mazur (private comunication).