AIP | Journal of Mathematical Physics

Nonequilibrium fluctuations in driven systems

B. H. Lavenda

Citation: Journal of Mathematical Physics **21**, 1826 (1980); doi: 10.1063/1.524636
View online: http://dx.doi.org/10.1063/1.524636
View Table of Contents: http://scitation.aip.org/content/aip/journal/jmp/21/7?ver=pdfcov
Published by the AIP Publishing

Nonequilibrium fluctuations in driven systems

B. H. Lavenda
TEMA S.P.A., Via Marconi 29/1, 40122 Bologna and Istituto di Fisica Sperimentale, Via Tari 3, Napoli, Italy,

(Received 4 May 1979; accepted for publication 19 November 1979)

The validity of a fluctuation-dissipation theorem for nonequilibrium fluctuations in driven systems is discussed. It is found that the Gaussian assumption alone does not necessarily lead to a fluctuation-dissipation theorem but rather the Markov property must also be invoked. Consequences of the Gaussian–Markov assumption are: (i) the spectral density reduces to a sum of two independent contributions, one due to internal noise and the other to external excitations; and (ii) the mode of regression of nonequilibrium fluctuations is identical to the decay of fluctuations to equilibrium. Without the Markov assumption, time-varying external fields can induce additional correlations which: (i) influence the regression of fluctuations; and (ii) invalidate the fluctuation-dissipation theorem.

1. INTRODUCTION AND SUMMARY

One of the cornerstones of nonequilibrium statistical mechanics is the fluctuation-dissipation (FD) theorem[1] which represents a generalization of Nyquist's theorem[2] to nonequilibrium thermodynamic processes. Nyquist's theorem relates the electromotive force due to thermal agitation of electrons in a conductor to the resistive properties of the circuit. This is to say that the power spectrum or spectral density of the noise, $S(\epsilon;\omega)$, due to a fluctuating emf, ϵ, is related to the real part of the complex impedance $Z(\omega)$ by the formula

$$S(\epsilon,\omega) = 4k_B T{\cdot}\mathrm{Re}Z(\omega),$$

where k_B is Boltzmann's constant and T is the absolute temperature. The generalization of Nyquist's theorem, commonly referred to as the fluctuation-dissipation theorem, states that the change in the state of a system due to the action of an external (or fluctuating) force is accompanied by the absorption of energy whose rate is equal to that at which the energy is dissipated in the system.

There is, however an ambiguity to the FD theorem in that it apparently makes no difference as to whether the fluctuations occur spontaneously from equilibrium, i.e., internal noise, or whether they are the result of an imposed constraint. Let us recall that the Callen–Welton[1] derivation of the FD theorem requires the action of an external force, yet, the same results can be obtained by considering spontaneous fluctuations that are formally caused by the action of fictitious "random" forces.[3] That the system be insensitive to the way in which fluctuations occur is not intuitively obvious; Onsager and Machlup[4] have pointed out that this is, indeed, a very strong postulate: for a Gaussian process, it can be shown to be equivalent to the Markov assumption. Moreover, it is not self-evident that a FD theorem should be valid for systems in which fluctuations are caused by both random forces and external, time-varying constraints.[5]

We preface our remarks by clearly stating the limitations of our analysis. The first and foremost limitation is that the FD theorem is not valid beyond the linear approximation,[6] if the process happens to be nonlinear. This is to say that fluctuations in the emf need to be so small that nonlinear terms are unimportant. We shall guarantee this by treating a linear process so that there will always be present a Nyquist noise with an equilibrium temperature. In the Langevin description of a random process, in terms of noise sources (cf Sec. 2), the assumption that the random force is a Gaussian random variable together with the linearity of the process implies that the process is normal.

Within this limiting framework, we show that on account of the Gaussian–Markov postulate, we may carry over many of the equilibrium results to nonequilibrium fluctuations in driven systems. In particular, we obtain a FD theorem for the internal noise contribution to the spectral density even for slow, nonstationary processes for which it still makes sense to define a spectral density. We show that for Gaussian processes, the Markov assumption reduces the total spectral density to a sum of two, *independent* contributions: one due to internal noise for which there exists a FD theorem, relating the central second moments of the fluctuating variables to the dissipative properties of the system, and another contribution to the spectral density due to excitations that are caused by a time-varying, but otherwise arbitrary, external force. In other words, we show that the Gaussian assumption alone does not necessarily guarantee the validity of the FD theorem.

The FD theorem establishes a power balance between the rate at which energy is absorbed by the system and the rate at which energy is dissipated in the system. In physical terms, we may say that the system does not have the capacity to "store" energy (cf. Sec. 4), so that there cannot be noninstantaneous responses to external perturbations. This is guaranteed by the Markov assumption. We therefore conclude that for Gaussian processes, the Markov assumption is also required to ensure the existence of a FD theorem. Alternatively, for non-Gaussian–Markov processes, we are no longer able to express the spectral density as a superposition of internal noise and external excitations. Consequently, a FD theorem is no longer expected to hold.

Intuitively, we may say that regardless of whether fluctuations are occurring from an equilibrium or a nonequilibrium state, provided the process is Gaussian and the system does not remember how it got into the given state (i.e., the

 0022-2488/80/071826-07$1.00

Markov property), there exists a FD theorem and the regression of fluctuations is not influenced by time-varying, external constraints.

The latter statement can be considered as a generalization of the Onsager regression hypothesis to time-varying, external forces. We recall that the Onsager regression hypothesis states that the regression of spontaneous fluctuations obeys, *on the average*, the deterministic (phenomenological) law for the decay from the same nonequilibrium state back to equilibrium, when it has been produced by a constraint which is suddenly released.[7] Implicit in Onsager's hypothesis are: (i) the Markov assumption—the inability of the system to remember and (ii) the Gaussian assumption—the identification of the average with the most probable behavior. A regression theorem for Markov processes has been given by Lax[8] which does not make use of the Gaussian assumption. The utility of Lax's regression theorem is that it generalizes the Markov property from classical to quantum-mechanical systems by providing an appropriate factorization of the multitime density matrix. Limiting ourselves to the analysis of random processes that are both Markovian and Gaussian, which according to the generalized Doob theorem[9] must be linear Fokker–Planck processes (cf. Sec. 3), we find that the regression of fluctuations to a nonequilibrium-steady state in driven systems is identical to the regression of fluctuations to the state of equilibrium. This leads us to believe that Gaussian–Markov processes behave as if they were in equilibrium with respect to certain degrees of freedom while other degrees of freedom may be in a nonequilibrium state.

In Sec. 2 we briefly remark on the generalization of the Wiener–Khintchin theorem to slow, nonstationary processes. We then evaluate the autocorrelation function under nonequilibrium conditions by a method alternative to that of the characteristic function.[10] Under the Gaussian–Markov assumption, we find that fluctuations regress to a nonequilibrium steady state, or slowly evolving state, in the same way that they regress to the state of equilibrium. However, as a result of time-varying external fields, the mean value of the fluctuating variable is time-dependent and there will be an additional contribution to the spectral density at nonzero frequency due to external excitations. In order to gain an understanding of why external excitations have no effect on the regression of fluctuations, we perform a perturbation analysis in Sec. 3, using the path integral formulation of Gaussian nonequilibrium processes.[11,12] We find that the time-varying external field destroys the principle of microscopic reversibility since it can only create excitations and has no influence on the reverse transitions.

Finally, in Sec. 4 we show that, granting the Gaussian assumption, it is the Markov assumption that is responsible for our finding that the regression of fluctuations is not influenced by time-varying external fields. This is accomplished by comparing our results of Sec. 3 with those of a forced harmonic oscillator, to which we apply the operator formulation of nonequilibrium statistical thermodynamics.[12] We observe that the external field causes virtual transitions to and from neighboring excited states in the forced harmonic oscillator and this influences the way in which fluctuations regress. Moreover, the Markov assumption is violated since the system now remembers how it got into a given state. And on account of the fact that the system can store energy in the field, all responses need not be instantaneous; the system can manifest noninstantaneous responses to external perturbations.

2. THE WIENER–KHINTCHIN THEOREM FOR SLOW, NONSTATIONARY PROCESSES

The Wiener[13]–Khintchin[14] theorem relates the spectral density $S(\alpha;\omega)$ of a *stationary*, random process $\alpha(t)$ to the autocorrelation function $C(t)$ through a Fourier cosine transform:

$$S(\alpha;\omega) = 4\int_0^\infty C(t)\cos\omega t\, dt. \tag{2.1}$$

The derivation of (2.1) makes use of the property that the statistical characteristics of the random process are invariant under time translations. A generalization of the theorem to slow, nonstationary processes can be achieved under the conditions that the mean value $m(t) = \langle \alpha(t)\rangle$ and the autocovariance $A(t) = \langle [\alpha(t) - m(t)][\alpha(0) - m(0)]\rangle$ change slightly over times of the order of the correlation time τ_c, defined as

$$\tau_c \equiv \int_{-\infty}^{\infty} \tau A(\tau)\, d\tau \Big/ \int_{-\infty}^{\infty} A(\tau)\, d\tau. \tag{2.2}$$

This is to say that a spectral density may be defined as

$$S(\alpha;\omega,t) = 2\int_{-\infty}^{\infty} C(t,t+\tau)e^{-i\omega\tau}\, d\tau, \tag{2.3}$$

provided the following conditions are fulfilled[15]:

$$\tau_c \frac{dm}{dt} \ll m \quad \text{and} \quad \tau_c \frac{dA}{dt} \ll A. \tag{2.4}$$

The major difference between the stationary and slow, nonstationary definitions of the spectral density, (2.1) and (2.3) respectively, is that in the latter case, the autocorrelation function depends not only on the time difference but also upon the absolute time. In Sec. 3 we shall see that conditions (2.4) require the external force to vary slowly over times of the order of the inverse of the damping constant. Our analysis of fluctuations that occur in slow, nonstationary processes is now directed to the evaluation of the autocorrelation function appearing in (2.3).

Hashitsume[10] was probably the first to note the somewhat curious fact that time-varying exernal forces, acting on *linear* systems, have no influence on the autocovariance expression describing the regression of fluctuations. He analyzed the case of Brownian motion of a driven harmonic oscillator and found that the expression for the autocovariance was not modified by a time-varying electric field. Since this finding will be shown to be due to the Gaussian–Markov assumptions, it will suffice us to analyze the stochastic differential equation:

$$R\dot{\alpha} + s\alpha = X(t) + x(t). \tag{2.5}$$

By writing down Eq. (2.5), we have taken a Langevin description of the linear random process $\alpha(t)$, in which the noise source that generates the process is represented by the random force $x(t)$. In the absence of the random force, Eq. (2.5) describes, for example, an RC circuit with an external emf, $X(t)$. We assume, for generality, that the external force is time-varying but is otherwise completely arbitrary.

In the Langevin noise source formulation, the fluctuating force is taken to represent thermal noise which is always stationary with a uniform spectrum. In order to be consistent with the fact that Eq. (2.5) describes, on the average, the deterministic evolution of the system, it is essential to assume that the conditional mean of the random force vanishes:

$$\langle x(t)\rangle_{\alpha_0} = 0, \quad t > t_0, \tag{2.6}$$

for any given initial value α_0. The Markovian property arises from the condition that the correlation function of the fluctuating force at two different times vanishes. In order to have a random process, it is necessary to assume that there is a sudden change in behavior at $t = t_0$, or, in other words, that the fluctuating force is δ-correlated

$$\langle x(t)x(t_0)\rangle = 2D\delta(t - t_0), \tag{2.7a}$$

where D is the diffusion coefficient, given by the Einstein relation:

$$D = k_B R^{-1}. \tag{2.7b}$$

Finally, the property that α is Gaussian follows from the observations that the average of the fluctuating forces over short time intervals is normal and that the process is linear.

The autocorrelation function is defined as

$$C(t,t_0) \equiv \langle \alpha(t)\alpha(t_0)\rangle, \tag{2.8}$$

where the angular brackets mean

$$\langle \alpha(t)\alpha(t_0)\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \alpha_0\alpha\omega_2(\alpha,\alpha_0)\, d\alpha\, d\alpha_0, \tag{2.9}$$

subject to $\alpha = \alpha(t)$ and $\alpha_0 = \alpha(t_0)$. It is important to bear in mind that we make no reference to an equilibrium ensemble in defining (2.8), as in the Kadanoff–Martin[16] definition of the equilibrium time correlation function.

In order to evaluate the autocorrelation function, we must first determine the two-joint probability density function (pdf), $\omega_2(\alpha,\alpha_0)$. Our task is simplified considerably by invoking the Markov assumption [cf. (2.7a)]. We can then write the two-joint pdf as a product of the conditional pdf $\omega_1(\alpha,t\,|\alpha_0,t_0)$ and the single pdf $\omega_0(\alpha_0)$, viz.,

$$\omega_2(\alpha,\alpha_0) = \omega_1(\alpha,t\,|\alpha_0,t_0)\cdot\omega_0(\alpha_0). \tag{2.10}$$

Substituting (2.10) into (2.9) reduces the autocorrelation function to a single integral

$$\langle \alpha(t)\alpha(t_0)\rangle = \int_{-\infty}^{\infty} \langle \alpha(t)\rangle_{\alpha_0}\alpha_0\omega_0(\alpha_0)\, d\alpha_0, \tag{2.11}$$

where $\langle \alpha(t)\rangle_{\alpha_0}$ is the conditional average:

$$\langle \alpha(t)\rangle_{\alpha_0} = \int_{-\infty}^{\infty} \alpha\omega_1(\alpha,t\,|\alpha_0,t_0)\, d\alpha. \tag{2.12}$$

We now have to evaluate the two-joint pdf (2.10).

Rather than employing the method of characteristic functions[10] to evaluate the pdf, we choose the more intuitive method of solving the Fokker–Planck equation

$$\frac{\partial}{\partial t}\omega = \frac{\partial}{\partial \alpha}\{(\gamma\alpha - X(t)/R)\omega\} + D\frac{\partial^2\omega}{\partial\alpha^2}, \tag{2.13}$$

where $\gamma = s/R$ and ω is any member of the hierarchy of pdf.

The explicit evaluation of any pdf from the Fokker–Planck equation depends on the imposed initial and boundary value conditions. Solving the Fokker–Planck equation (2.13) subject to the condition

$$\omega = \delta(\alpha - \alpha_0) \quad \text{for } t = 0, \tag{2.14}$$

say, by the method of variation of parameters,[17] we obtain the expression

$$\omega_1(\alpha,t\,|\alpha_0,0) = \{2\pi k_B[1 - \exp(-2\gamma t)]/s\}^{-1/2} \times \exp(-Q/2k_B), \tag{2.15}$$

for the conditional pdf, where

$$Q = s|\alpha - \alpha_0 e^{-\gamma t} - R^{-1} \times \int_0^t \exp[-\gamma(t-u)]X(u)\, du|^2/(1 - e^{-2\gamma t}). \tag{2.16}$$

If we allow a long enough time to elapse, it is natural to suppose that the system will forget its initial condition and the conditional pdf will go over into the single pdf. Assuming that the system has evolved from the state $\alpha_0 = 0$ at some very distance time in the past, $t_0 = -\infty$, due to the action of a time-varying, external force, we obtain the solution to the Fokker–Planck equation:

$$\omega_\infty(\alpha,t) = (s/2\pi k_B)^{1/2}\exp\left\{-s|\alpha - R^{-1} \times \int_{-\infty}^t \exp[-\gamma(t-u)]X(u)\, du|^2/2k_B\right\}, \tag{2.17}$$

which is the single pdf of the "aged" system. It should be noticed that (2.17) does not coincide with either a stationary $X =$ const, or an equilibrium, $X = 0$, pdf. For slow, nonstationary processes, however, (2.17) will play the role of the single pdf in the autocorrelation function expression, (2.11). Now inserting expressions (2.15) and (2.17) into (2.10) and then into (2.9), we obtain the expression for the autocorrelation function:

$$\begin{aligned} C(t,t_0) = {} & (k_B/s)\exp[-\gamma(t-t_0)] \\ & + \left\{R^{-1}\int_{-\infty}^t \exp[-\gamma(t-u)]X(u)\, du\right\} \\ & \times \left\{R^{-1}\int_{-\infty}^{t_0} \exp[-\gamma(t_0-u)]X(u)\, du\right\}. \end{aligned} \tag{2.18}$$

The autocorrelation function and autocovariance are related by

$$A(t) = C(t) - m^2(t). \tag{2.19}$$

Knowing that

$$m(t) = R^{-1}\int_{-\infty}^t \exp[-\gamma(t-u)]X(u)\, du, \tag{2.20}$$

which is a particular solution of the deterministic equation associated with the stochastic differential equation (2.5), we get the expression for the autocovariance from (2.19):

$$A(t-t_0) = (k_B/s)\exp[-\gamma(t-t_0)]. \qquad (2.21)$$

From this result, we conclude that for Gaussian–Markov processes, fluctuations regress in driven systems in exactly the same way as they do to the state of equilibrium. In other words, it shows that time-varying, external forces have no influence on the regression of fluctuations in Gaussian–Markov processes.

The spectral density, (2.3), can now be computed by taking the Fourier transform of the autocorrelation function, (2.18). We then obtain

$$S(\alpha;\omega,t_0) = S(\alpha - m;\omega) + S(X;\omega,t_0), \qquad (2.22)$$

where the contribution of the internal noise to the spectral density is still given by Nyquist's theorem

$$\omega^2 S(\alpha - m;\omega) = 4k_B T\cdot \mathrm{Re}\, Y(\omega), \qquad (2.23)$$

where $Y(\omega)$ is the admittance

$$Y(\omega) = (R + s/i\omega)^{-1}/T. \qquad (2.24)$$

The important result which follows from (2.22) is that for Gaussian–Markov processes, the total spectral density is the sum of two, independent contributions: one coming from internal noise and the other from external excitations.

In the particular case of stationary, periodic excitations, $X(t) = X_0\exp(i\omega_0 t)$, the spectral density (2.22) reduces to

$$\omega^2 S(\alpha;\omega) = 4k_B T\cdot\mathrm{Re}\, Y(\omega) + 4\pi R^{-1}|X_0|^2 \times \mathrm{Re}\, Y(\omega_0)\delta(\omega+\omega_0). \qquad (2.25)$$

In words, (2.25) states that periodic, external excitations will only contribute to the noise spectrum when they are in resonance with the natural frequencies of the system. In view of this result, it is interesting to recall Richardson's[5] conjecture that there need be no connection between the admittance function that describes the regression of fluctuations and the response of the system to external excitations. Expression (2.25) shows that the admittance functions must be identical for periodic, stationary excitations.

To conclude this section, we compare our results with those of Lax.[18] Lax took into account that fluctuations were occurring from a nonequilibrium steady state implicitly through the values of the coefficients in the Langevin equation. He then proposed that a Nyquist relation for nonequilibrium fluctuations be given by

$$\omega^2 S(\alpha;\omega) = 4k_B T\cdot\mathrm{Re}\, Y(\omega)\eta, \qquad (2.26)$$

where η is the correction factor:

$$\eta = (s/k_B)\langle\alpha^2\rangle, \qquad (2.27)$$

measuring the deviation from equilibrium where $\eta = 1$. Lax's analysis applies to fluctuations from a nonequilibrium steady state which is maintained by time-independent external constraints. The spectral density of such processes is given by

$$S(\alpha;\omega) = S(\alpha - m;\omega) + 4\pi m^2\delta(\omega). \qquad (2.28)$$

The δ function in the second term is due to the fact that the condition of stationariness requires the mean value to be independent of time. From expression (2.28), we observe that the only difference in the spectral density of fluctuations occurring from equilibrium or a nonequilibrium steady state, maintained by time-independent external constraints, is a shift in the power spectrum. We therefore conclude that the case of time-independent external constraints is uninteresting since there are no qualitative differences in the spectral density for fluctuations occurring from equilibrium or a nonequilibrium steady state. Our approach differs from that of Lax's in that we have taken the constraints, which are now time-dependent, explicitly into account.

3. TIME-DEPENDENT TRANSITION PROBABILITIES

In the last section, we gave the conditions for which a spectral density can be defined for slow, nonstationary processes [cf. conditions (2.4)]. Considering the solution of the averaged Langevin equation, in which $\langle x(t)\rangle_{\alpha_0} = 0$, we observe that conditions (2.4) will be satisfied provided the external force varies slightly over times of the order of γ^{-1}. In this event, we can treat the external force as a small, time-dependent perturbation and apply time-dependent perturbation theory to the Fokker–Planck equation (2.13).

The Fokker–Planck equation may be formally written in the operator form:

$$\frac{\partial\omega}{\partial t} = (2k_B)^{-1}\hat{F}\omega, \qquad (3.1)$$

where the symbol "$\hat{\ }$" is used to distinguish an operator from an ordinary function. Rather than studying the properties of the Fokker–Planck operator $\hat{F}$, it will prove advantageous to apply the "gradient transformation"[19]

$$\omega(\alpha,t) = \exp\left(-s\int \alpha\, d\alpha/2k_B\right)\cdot\phi(\alpha,t), \qquad (3.2)$$

where[20]

$$\int \alpha\, d\alpha = \tfrac{1}{2}\alpha^2 - \tfrac{1}{2}\langle\alpha^2\rangle, \qquad (3.3)$$

to Eq. (3.1) and study the properties of the Hamiltonian operator $\hat{H}$, defined by the Schrödinger-type equation:

$$\frac{\partial\phi}{\partial t} = -(\tfrac{1}{2}\gamma)\left(\frac{\gamma R\alpha^2}{2k_B} - \frac{X(t)\alpha}{k_B}\right)\phi - \frac{X(t)}{R}\cdot\frac{\partial\phi}{\partial\alpha} + \frac{k_B}{R}\cdot\frac{\partial^2\phi}{\partial\alpha^2} \equiv (\tfrac{1}{2}k_B^{-1})\hat{H}\phi. \qquad (3.4)$$

For a vanishing external force, Eq. (3.4) becomes identical to the Schrödinger equation for a harmonic oscillator. This would lead us to suppose that for a small external force, the Hamiltonian $\hat{H}$ can be decomposed into an unperturbed part $\hat{H}_0$ and a perturbed part $\hat{H}_1$:

$$\hat{H} = \hat{H}_0 + \hat{H}_1. \qquad (3.5)$$

$\hat{H}_0$ is a self-adjoint operator and possesses a complete set of eigenfunctions that correspond to those of a harmonic oscillator, viz.,

$$\phi_n = (2^n n!)^{-1/2}(s/2\pi k_B)^{1/4}H_n(\xi)\exp(-\tfrac{1}{2}\xi^2), \qquad (3.6)$$

where

$$\xi = (s/2k_B)^{1/2}\alpha, \quad \text{and} \quad H_n(\xi) = (-1)^n\left(e^{\xi^2}\frac{d^n}{d\xi^n}e^{-\xi^2}\right), \tag{3.7}$$

i.e., H_n is the nth degree Hermite polynomial.

The transformed Fokker–Planck equation, (3.4), is comparable to the Schrödinger equation of a forced harmonic oscillator (cf. Sec. 4) in the presence of a vector potential. In analogy with the Feynman path integral formulation of quantum electrodynamics,[21] we define a kernel $G(\alpha,t\,|\alpha_0,t_0)$ which propagates the function ϕ from one point in α-space and time to another point at a later time according to the integral equation[12]

$$\phi(\alpha,t) = \int_{-\infty}^{\infty} G(\alpha,t\,|\alpha_0,t_0)\phi(\alpha_0,t_0)\,d\alpha_0. \tag{3.8}$$

This integral equation bears a striking resemblance to the Chapman–Kolmogorov equation and it is a consequence of the Markov assumption. In the absence of the external force, the perturbed Hamiltonian $\hat{H}_1$ vanishes and the kernel can be expanded as a bilinear sum of orthonormal functions, (3.6), multiplied by exponential decaying functions of time[12]

$$G_0(\alpha,t\,|\alpha_0,t_0) = \sum_{n=0}\phi_n(\alpha)\phi_n(\alpha_0)\exp[-\Gamma_n(t-t_0)], \tag{3.9}$$

with $\Gamma_n = n\gamma$. In the presence of time-varying external fields, the time dependence will no longer be given by a simple exponential factor and instead we write:

$$G(\alpha,t\,|\alpha_0,t_0) = \sum_{m=0}\sum_{n=0}\lambda_{nm}(t,t_0)\phi_n(\alpha)\phi_m(\alpha_0), \tag{3.10}$$

where the time-dependent transition probabilities $\lambda_{nm}(t,t_0)$ have now to be determined.

We express the kernel in the path integral form[12]

$$G(\alpha,t\,|\alpha_0,t_0) = \overline{\int\!\!\int}\exp\left[-(2k_B)^{-1}\int_{t_0}^{t}L(\alpha,\dot{\alpha},t)\,dt\right]D\alpha. \tag{3.11}$$

The connected integral sign denotes an average over all possible paths which begin in state α_0 at time t_0 and terminate in state α at the later time t. The Lagrangian L, in the present case, is

$$L(\alpha,\dot{\alpha},t) = \tfrac{1}{4}R\,\{(\dot{\alpha}-X(t)/R)^2 + \gamma^2\alpha^2 - 2\gamma\alpha X(t)/R\}, \tag{3.12}$$

which is seen to be a combination of the Lagrangian of a charged particle in an electromagnetic field and a forced harmonic oscillator. We could now apply time-dependent perturbation theory by expanding the exponential in (3.11) as a power series in the external force and calculate the time-dependent transition probabilities to any desired order in the external force.[22] However, if we note that our process is Gaussian and formally corresponds to a forced harmonic oscillator, which can be solved in closed form,[21] then we realize that the transition probabilities are also obtainable in closed form.

Using the Gaussian property, we equate average and most probable values so that the path average of the negative exponential of the action[11]

$$A = \int_{t_0}^{t}L(\alpha,\dot{\alpha},t)\,dt, \tag{3.13}$$

in expression (3.11) for the kernel can be replaced by

$$G(\alpha,t\,|\alpha_0,t_0) \propto \exp\left\{-(2k_B)^{-1}\left[\int_{t_0}^{t}L(\alpha,\dot{\alpha},t)\,dt\right]_{\min}\right\}. \tag{3.14}$$

Thus, the Lagrangian must satisfy the Euler–Lagrange equation:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial\dot{\alpha}}\right) - \frac{\partial L}{\partial\alpha} = 0 \quad\text{or}\quad \ddot{\alpha} - \gamma^2\alpha = R^{-1}(\dot{X} - \gamma X), \tag{3.15}$$

which is similar to the equation of motion of a forced harmonic oscillator. The relation between the Euler–Lagrange equation, (3.15), which is a necessary condition for the extremum of the action (3.13), and the averaged Langevin equation can be deduced by writing the Euler–Lagrange equation (3.15) in canonical form.

Defining the conjugate momentum variable β in the usual fashion,

$$\beta \equiv \frac{\partial L}{\partial\dot{\alpha}}, \tag{3.16}$$

and taking the Legendre transform of the Lagrangian (3.12) with respect to the velocity, we obtain the Hamiltonian:

$$H(\alpha,\beta) = \frac{\partial L}{\partial\dot{\alpha}}\dot{\alpha} - L = \beta\dot{\alpha} - L, \tag{3.17}$$

whose corresponding operator has already been defined by Eq. (3.4) using the "quantization" condition[23]

$$\hat{\beta} = -2k_B\frac{\partial}{\partial\alpha}. \tag{3.18}$$

The canonical form of the Euler–Lagrange equation (3.13) is now given by the pair of equations:

$$\dot{\alpha} = \frac{\partial H}{\partial\beta} \quad\text{and}\quad \dot{\beta} = -\frac{\partial H}{\partial\alpha}. \tag{3.19}$$

Introducing the linear transformation

$$\xi = \tfrac{1}{2}(\alpha - \beta/s), \quad \eta = \tfrac{1}{2}(\alpha + \beta/s), \tag{3.20}$$

the canonical equations (3.19) are converted into the desired form:

$$\dot{\xi} + \gamma\xi = R^{-1}X(t), \tag{3.21}$$

$$\dot{\eta} - \gamma\eta = 0. \tag{3.22}$$

Equation (3.21) will be recognized readily as the averaged Langevin equation. In the case of a vanishing external force, the two equations are mirror images of one another; the general solution is a superposition of decaying and growing exponentials that manifest a symmetry in past and future.[24] The presence of the external force destroys this symmetry and also the reversibility of transitions between any two nonequilibrium states. We shall now investigate this symmetry breaking in greater detail.

Setting $\tau = t - t_0$, we write the general solution of the

Euler–Lagrange equation (3.15) as

$$\alpha(\tau) = \alpha_0 \cosh\gamma\tau + (\dot{\alpha}_0/\gamma)\sinh\gamma\tau + R^{-1} \times \int_0^\tau X(t)\exp[-\gamma(\tau - t)]\,dt. \quad (3.23)$$

The time integration in (3.13) can now be performed explicitly and we find

$$A = (s/2\sinh\gamma\tau)[(\alpha^2 + \alpha_0^2)\cosh\gamma\tau - 2\alpha\alpha_0 + 2(\alpha_0 - \alpha e^{\gamma\tau})\Phi + e^{\gamma\tau}\Phi^2], \quad (3.24)$$

where

$$\Phi = R^{-1}\int_0^\tau \exp[-\gamma(\tau - t)]X(t)\,dt. \quad (3.25)$$

The kernel can thus be written in the closed form:

$$G(\alpha,\tau|\alpha_0,0) = (se^{\gamma\tau}/4\pi k_B \sinh\gamma\tau)^{1/2}\exp(-A/2k_B). \quad (3.26)$$

The time-dependent transition probabilities in expression (3.10) are now obtainable by multiplying it by $\phi_n(\alpha)$ and $\phi_m(\alpha_0)$ and integrating over all α and α_0. The result can be written in the form of a matrix element of the kernel

$$\lambda_{nm}(\tau) = \langle\phi_n(\alpha)|G(\alpha,\tau|\alpha_0,0)|\phi_m(\alpha_0)\rangle. \quad (3.27)$$

Of particular interest is the probability of transition from the equilibrium or "ground" state to the first excited state which we shall refer to as the $0\to1$ transition. The transition probability is:

$$\lambda_{10}(\tau) = \langle\phi_1(\alpha)|G(\alpha,\tau|\alpha_0,0)|\phi_0(\alpha_0)\rangle = (s/k_B)^{1/2}\Phi. \quad (3.28)$$

Calculating the transition probability for the reverse transition, i.e., the $1\to0$ transition, we obtain the surprising result that $\lambda_{01}(\tau)$ vanishes. This implies that time-varying external fields destroy the principle of microscopic reversibility which equates the frequencies of forward and reverse transition at equilibrium.[25] In Sec. 4, we shall see that this symmetry breaking is due to the Markov assumption which, for Gaussian processes, means that the system does not remember how it got into the given state.

If the reverse transition probabilities did not vanish, then the virtual transitions to other states could take place leading to a modification of the autocovariance expression (2.21). That is, the transition probability for the decay of a fluctuation from the first excited state would be given by

$$\lambda_{11}(\tau) = \langle\phi_1(\alpha)|G(\alpha,\tau|\alpha_0,0)|\phi_1(\alpha_0)\rangle + \sum_n \langle\phi_1(\alpha)|G(\alpha,\tau|\alpha',t)|\phi_n(\alpha')\rangle \times\langle\phi_n(\alpha')|G(\alpha',\tau|\alpha_0,0)|\phi_1(\alpha_0)\rangle, \quad (3.29)$$

with $\tau > t \geqslant 0$. In expression (3.29), we have introduced a complete set of states to take into account virtual transitions. Due to the finding that the transition probabilities of all reverse transitions vanish, expression (3.29) gives the correct temporal dependence of the autocovariance (2.21), viz.,

$$\lambda_{11}(\tau) = \langle\phi_1(\alpha)|G(\alpha,\tau|\alpha_0,0)|\phi_1(\alpha_0)\rangle = \exp(-\gamma\tau). \quad (3.30)$$

Therefore, for Gaussian process that are also Markovian, we find that although time-varying, external fields create excitations, they have no influence on the decay of a fluctuation from a given state.

4. ELEMENTARY EXCITATIONS IN NONSTATIONARY PROCESSES

In this section, we show by comparison with the forced harmonic oscillator, that the inability of time-varying external fields to influence the decay of a fluctuation from a given nonequilibrium state is due to the Markov property. In Sec. 3 we treated the external field as a perturbation in a Schrödinger-type equation describing a harmonic oscillator. In analogy with quantum field theory, it would appear advantageous to introduce the creation and annihilation operators of second quantization[12]

$$\hat{a}^\dagger = \left(\frac{k_B}{s}\right)^{1/2}\left(\frac{s\alpha}{2k_B} - \frac{\partial}{\partial\alpha}\right), \quad (4.1)$$

$$\hat{a} = \left(\frac{k_B}{s}\right)^{1/2}\left(\frac{s\alpha}{2k_B} + \frac{\partial}{\partial\alpha}\right). \quad (4.2)$$

It is easily seen that these operators obey the commutation relations for Bose particles.

In terms of the creation and annihilation operators, the Hamiltonian of the transformed Fokker–Planck equation (3.4) is

$$(2k_B)^{-1}\hat{H} = \gamma\hat{a}^\dagger\hat{a} - (s/k_B)^{1/2}R^{-1}X(t)\hat{a}^\dagger, \quad (4.3)$$

which bears a striking resemblance to the Hamiltonian of a forced harmonic oscillator

$$(2k_B)^{-1}\hat{H}_f = \gamma\hat{a}^\dagger\hat{a} - (s/k_B)^{1/2}R^{-1}X(t)(\hat{a} + \hat{a}^\dagger). \quad (4.4)$$

The Hamiltonian (4.3) can be used to derive the Heisenberg equations of motion for the annihilation and creation operators, viz.,

$$\frac{d\hat{a}}{dt} = (2k_B)^{-1}[\hat{H},\hat{a}] = -\gamma\hat{a} + \left(\frac{s}{k_B}\right)^{1/2}R^{-1}X(t), \quad (4.5)$$

$$\frac{d\hat{a}^\dagger}{dt} = (2k_B)^{-1}[\hat{H},\hat{a}^\dagger] = \gamma\hat{a}^\dagger. \quad (4.6)$$

These equations of motion are analogous to the pair of canonical equations (3.21) and (3.22). Their solutions are

$$\hat{a}(t) = \exp(-\gamma t)\hat{a} + (s/k_B)^{1/2}R^{-1} \times \int_{-\infty}^t \exp[-\gamma(t-u)]X(u)\,du, \quad (4.7)$$

$$a^\dagger(t) = \exp(\gamma t)\hat{a}^\dagger, \quad (4.8)$$

which clearly display the asymmetry caused by the external field in the creation and destruction of elementary excitations.

The time dependencies of these operators can be written in a more compact form by defining the operators,

$$\hat{S}_0 = \exp(-\gamma\hat{a}^\dagger\hat{a}t), \quad (4.9)$$

$$\hat{S}_1 = \exp(\Xi^{(+)}\hat{a}), \quad (4.10)$$

with

$$\Xi^{(+)} = (s/k_B)^{1/2}R^{-1}\int_{-\infty}^t \exp(\gamma u)X(u)\,du. \quad (4.11)$$

With the aid of these operators, the solutions of the equations of motion, (4.7) and (4.8), can be written in the generic form

$$\hat{A}(t) = \hat{U}^{-1}(t)\hat{A}\hat{U}(t), \quad (4.12)$$

for any operator $\hat{A}$ and $\hat{U}(t)$ is the time development operator,

$$\hat{U}(t) \equiv \hat{S}_0 \hat{S}_1. \tag{4.13}$$

We are now in a position to express the moments as expectation values of particular combinations and products of the creation and annihilation operators over the ground state $|0\rangle = \phi_0$. Likewise, ϕ_1 corresponds to the first excited state, $|1\rangle$, and so on. The mean value $m(t)$ is given by the expectation value

$$m(t) = (k_B/s)^{1/2}\langle 0|\{\hat{a}(t) + \hat{a}^\dagger(t)\}|0\rangle$$
$$= (k_B/s)^{1/2}\langle 0|\hat{U}^{-1}(t)\hat{a}\hat{U}(t)|0\rangle = (2.20). \tag{4.14}$$

The autocorrelation function is given by the expression

$$A(t) = (k_B/s)\langle 0|\hat{a}(t)\hat{a}^\dagger(0)|0\rangle$$
$$= (k_B/s)\langle 0|\hat{U}^{-1}(t)\hat{a}\hat{U}(t)\hat{a}^\dagger|0\rangle$$
$$= (k_B/s)\langle 0|\{\hat{a} + \Xi^{(+)}\}\hat{a}^\dagger|0\rangle \exp(-\gamma t) = (2.21). \tag{4.15}$$

The steps leading to the final result in (4.15) have been written out in detail in order to demonstrate that the external field has no influence on the decay of fluctuations from a given state. In the language of second quantization, we say that the operator $\Xi^{(+)}\hat{a}^\dagger$ does not have a conjugate operator $\Xi^{(-)}\hat{a}$ which would induce de-excitations. It will now be appreciated that, in comparison with the forced harmonic oscillator, the presence of the conjugate operator $\Xi^{(-)}\hat{a}$ is incompatible with the Markov assumption.

In the case of the forced harmonic oscillator, whose Hamiltonian is given by (4.4), the operator $\hat{S}_1$ in (4.10) must be replaced by

$$\hat{S}_{1f} = \exp[\tfrac{1}{2}(\Xi^{(+)}\hat{a}^\dagger + \Xi^{(-)}\hat{a})], \tag{4.16}$$

where

$$\Xi^{(-)} = (s/k_B)^{1/2}R^{-1}\int_t^\infty \exp(-\gamma u)X(u)\,du. \tag{4.17}$$

Following the same procedure, we now find the mean value and autocovariance are given by

$$m_f(t) = (2R)^{-1}\left\{\int_{-\infty}^t \exp[-\gamma(t-u)]X(u)\,du - \int_t^\infty \exp[\gamma(t-u)]X(u)\,du\right\}, \tag{4.18}$$

$$A_f(t) = (k_B/s)\exp(-\gamma t)\cdot\exp\left[-(\gamma/2k_BR)\int_{-\infty}^t du \times \int_t^\infty dv\,X(v)X(u)e^{-\gamma(v-u)}\right], \tag{4.19}$$

respectively. The autocovariance expression for the forced harmonic oscillator, (4.19), clearly shows that the time-varying external field has an "influence" on the decay of fluctuations from a given nonequilibrium state.

A result, similar to (4.19), was first obtained by Feynman[21] who used the forced harmonic oscillator as a model to study the interaction of charged particles with the electromagnetic field. Using his Lagrangian formulation of nonrelativistic quantum mechanics, Feynman found it possible to eliminate the coordinates of the field, considered as a set of uncoupled oscillators, and to recast the problem in terms of the coordinates of the particles alone. The effect of the field was to cause a delayed interaction between the particles and it was described by an "influence functional," similar to the second exponential factor in (4.19)[26]

The fact that the system now has the capability to store energy, as witnessed by noninstaneous responses to external perturbations, implies that the process has acquired a "memory" and is therefore no longer Markovian. The time-varying external field can now induce virtual transitions to and from neighboring excited states and these additional correlations manifest themselves in the mode of regression of fluctuations. Furthermore, since the system has the capacity to store energy, the power balance between the rate at which energy is absorbed by the system and the rate at which it is dissipated in the system, as required by the FD theorem, will no longer be fulfilled. Consequently, eventhough the process is Gaussian, a FD theorem will not be valid since it is no longer Markovian.

[1]H. B. Callen and J. H. Welton, Phys. Rev. **83**, 34 (1951). See also: R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).
[2]H. Nyquist, Phys. Rev. **32**, 110 (1928).
[3]L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1959), p. 393.
[4]L. Onsager and S. Machlup, Phys. Rev. **91**, 1505 (1953).
[5]J. Richardson, IRE Trans. Inf. Theory **IT-1**, 62 (1955).
[6]N. G. Van Kampen, Physica **26**, 585 (1960).
[7]L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).
[8]M. Lax, Phys. Rev. **157**, 213 (1967); **172**, 350 (1968).
[9]M. Lax, Rev. Mod. Phys. **38**, 359 (1966).
[10]N. Hashitsume, Prog. Theor. Phys. **15**, 369 (1956).
[11]B. H. Lavenda, Nuovo Cimento **7**, 229 (1977).
[12]B. H. Lavenda, F. Fittipaldi, and G. Peluso, Riv. Nuovo Cimento B **42**, 9 (1977).
[13]N. Wiener, Acta Acad. Sci. Hung. Math. **55**, 117 (1930); J. Math. Phys. (Cambridge, Mass.) **5**, 99 (1926).
[14]A. I. Khintchin, Ann. Math. **109**, 604 (1934).
[15]R. L. Stratonovich, *Topics in the Theory of Random Noise* (Gordon and Breach, New York, 1963), Vol. 1, p. 131.
[16]L. P. Kadanoff and P.C. Martin, Ann. Phys. (N.Y.) **24**, 419 (1963).
[17]R. P. Feynman, *Statistical Mechanics: A Set of Lectures* (Benjamin, Reading, Mass., 1972), p. 50.
[18]M. Lax, Rev. Mod. Phys. **32**, 25 (1960).
[19]I. M. Gel'fand and A. M. Yaglom, J. Math. Phys. **1**, 48 (1960).
[20]The presence of a correction term, $\frac{1}{2}\langle\alpha^2\rangle$, is due to the fact that the random variable $\alpha(t)$ is not of bounded variation and the integral must be interpreted in the stochastic sense of *Itô* as explained in J. L. Doob, *Stochastic Processes* (Wiley, New York, 1953), p. 443. The physical significance of the correction term has been discussed in B. H. Lavenda, Phys. Lett. A **71**, 304 (1979).
[21]R. P. Feynman, Rev. Mod. Phys. **20**, 367 (1948); Phys. Rev. **80**, 440 (1950).
[22]R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965), pp. 143ff.
[23]N. Saitô and M. Namiki, Prog. Theor. Phys. **16**, 71 (1956).
[24]B. H. Lavenda and E. Santamato, Lett. Nuovo Cimento **26**, 27 (1979); **26**, 505 (1979).
[25]R. C. Tolman, *Principles of Statistical Mechanics* (Oxford Univ. Press., Oxford, 1938), p. 163.

[26]Noninstantaneous interactions have also been found in coupled, linear irreversible processes that, on account of a wide time scale separation between a primary process and secondary processes, simulate a heavy Brownian particle moving in a field of lighter Brownian particles; see Ref. 12.