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1972 J. Phys. A: Gen. Phys. 5 1312

(http://iopscience.iop.org/0022-3689/5/9/005)

J. Phys. A: Gen. Phys., Vol. 5, September 1972. Printed in Great Britain.

The generalized Langevin equation

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MS received 22 March 1972

Abstract. The simple Langevin equation describes a process which is both Markovian and Gaussian. A generalization of the Langevin equation allows us to deal with processes which are projections of n-dimensional Gaussian–Markov processes. The results are formally equivalent to generalizations proposed by Kubo in 1966 provided the second fluctuation–dissipation theorem is assumed true. Molecular motion in liquids is discussed in general terms and it is concluded that these generalizations of the Langevin equation are not likely to be successful.

1. Introduction

In looking for generalizations of the Langevin equation, we must be aware of all the properties of the Langevin equation and we must choose which properties to retain in the generalized form. For this reason we begin by stating the important features of the Langevin method for dealing with Brownian motion. It is concluded that the Brownian motion is characteristically a Gaussian–Markov process and this is generalized to motions which are projections of n-dimensional Gaussian–Markov processes. The question of the type of probability distribution is very important and is related to the Maxwell–Boltzmann law for the distribution of velocities, essentially this means that the velocity is Gaussian at a given time. However all distributions for the velocity are not Gaussian in general and this is discussed with reference to molecular motion in liquids.

Before we start, it is perhaps worth re-issuing the warning that the correlation functions used throughout this paper contradict the assumption of stationarity at some stage so that it is unwise to assume stationarity of averages in general (see eg Kubo 1966 or Henery 1971).

2. Simple Langevin equation

When a large particle is immersed in a gas, it is subject to a great many collisions by gas molecules. These collisions give rise to a viscous damping force which, according to Stokes law, is proportional to the velocity of the particle so that the *macroscopic* law of motion for the particle is

$$\frac{\mathrm{d}V}{\mathrm{d}t}+\beta V = 0.$$

It is then assumed that the microscopic law of motion is the Langevin equation

$$\frac{dV}{dt}+\beta V = F$$

where F is a random force which is uncorrelated over times greater than τ_0. This lack of correlation between $F(t)$ and $F(t+\tau)$ for $\tau > \tau_0$ is essential in the elementary treatment and it gives rise to two basic properties of Brownian motion. The first of these is the exponential correlation function $R(\tau) = \langle V(t)V(t+\tau)\rangle = \langle V^2\rangle \exp(-\beta|\tau|)$, and the second is the Gaussian distribution functions for the velocity at a single time or multi-dimensional Gaussianity for the velocities at sets of times (Uhlenbeck and Ornstein 1930†). Indeed there is a connection between these two properties by virtue of Doob's theorem. This states that a one-dimensional Gaussian process is Markovian only when the correlation function $R(t)$ has the exponential form $R(t) = \exp(-\beta t)$. The Markov nature of the process arises from the fact that the evolution of the velocity is determined only by its instantaneous velocity, and the uncorrelated nature of the random force F.

With these assumptions, a complete description of the statistical properties of $V(t)$ is given when we give the mean and autocorrelation function. Of course, if we are not dealing with Gaussian processes, we would require more knowledge about the process, in general, moments of all orders would be required. A non-Gaussian process with an exponential correlation function is the random telegraph signal (Rice 1944, 1945).

In considering generalizations, it is clear that we must drop either Gaussianity or the Markovian property or the exponential correlation function. However there is the possibility of considering Markovian processes in multi-dimensional space, and by taking an appropriate projection of the multi-dimensional process we obtain a generalization of the Brownian motion capable of dealing with any given stochastic process to any required degree of accuracy.

The extension to a many-dimensional process which is Gaussian and Markovian is limited, by Doob's theorem, to mixtures of exponential correlation functions. Thus if $\boldsymbol{V}(t)$ is an N-dimensional column vector with components $V_1(t), V_2(t), \ldots, V_N(t)$ we form the autocorrelation function (which is an N by N matrix)

$$\boldsymbol{R}(\tau) = \langle \boldsymbol{V}(t)\boldsymbol{V}'(t+\tau)\rangle.$$

Then, according to Doob's theorem (Ming Chen Wang and Uhlenbeck 1945), $\boldsymbol{V}(t)$ is Gaussian and Markovian only if

$$\boldsymbol{R}(\tau) = \boldsymbol{R}(0)\exp(-\boldsymbol{B}\tau)$$

where $\boldsymbol{B}$ is a constant matrix which is in general not symmetric. From here on we will assume that the eigenvalues β_i of $\boldsymbol{B}$ are distinct and nonzero. In fact, if $\boldsymbol{V}(t)$ satisfies the generalized Langevin equation

$$\frac{d\boldsymbol{V}}{dt}+\boldsymbol{B}'\boldsymbol{V} = \boldsymbol{F}$$

then the autocorrelation function $\boldsymbol{R}(\tau)$ will be of the form required by Doob's theorem.

† The references Ming Chen Wang and Uhlenbeck (1945), Rice (1944, 1945) and Uhlenbeck and Ornstein (1930) are reprinted in N Wax (ed) 1954 *Selected papers on noise and stochastic processes* (New York: Dover).

To express $\boldsymbol{R}(\tau)$ as a sum of exponentials, it is necessary to find the eigenvalues β_i of the matrix $\boldsymbol{B}$. We can then construct a nonsingular matrix $\boldsymbol{A}$, consisting of the eigenvectors of $\boldsymbol{B}$, such that $\boldsymbol{A}^{-1}\boldsymbol{B}\boldsymbol{A}$ is diagonal with diagonal components equal to the β_i. With this simplification it is easily shown that

$$\begin{aligned}\boldsymbol{R}(\tau) &= \boldsymbol{R}(0)\boldsymbol{A}\exp(-\boldsymbol{A}^{-1}\boldsymbol{B}\boldsymbol{A}\tau)\boldsymbol{A}^{-1} \\ &= \boldsymbol{R}(0)\boldsymbol{A}\boldsymbol{E}(\tau)\boldsymbol{A}^{-1}\end{aligned}$$

where $\boldsymbol{E}$ is a diagonal matrix with elements $\exp(-\beta_i\tau)$.

In the next section we will consider an extension of the Langevin equation involving derivatives of $V(t)$ up to the nth. This equation can be solved using the standard device of transforming to a system of n first-order linear equations, thus bringing it within the scope of Doob's theorem and the process described will be Gaussian and Markovian. For example, the equation

$$\frac{\mathrm{d}^n y}{\mathrm{d}t^n} + b_{n-1}\frac{\mathrm{d}^{n-1}y}{\mathrm{d}t^{n-1}} + \ldots + b_0 y = F$$

may be transformed to the n equations

$$y_1 = \frac{\mathrm{d}y}{\mathrm{d}t}$$

$$y_2 = \frac{\mathrm{d}y_1}{\mathrm{d}t}$$

$$\ldots\ldots\ldots$$

$$\ldots\ldots\ldots$$

$$\frac{\mathrm{d}y_{n-1}}{\mathrm{d}t} + b_{n-1}y_{n-1} + \ldots + b_0 y = F$$

and these may be solved for the correlation functions using the technique described above. However, in this case a simpler method is available and the only use we will make of the previous theory is to show that all correlations are linear combinations of exponentials.

3. Generalizations

Two possible extensions of the Langevin equation are given in equations (1) and (2), and we will later consider a third possibility, which, although at first sight different from the first two, gives the same results in certain circumstances. In both (1) and (2) the force $F(t)$ is supposed to be correlated and, to simplify the later discussion, we will take the force autocorrelation function to be exponential (or a mixture of exponentials). To allow for the correlated structure of $F(t)$, the delayed viscous drag (given by the convolution terms in (1) and (2)) will depend on the velocity at all past instants so that the convolution integrals should both be extended to $t = -\infty$. However, by assuming that the behaviour described by (1) and (2) is independent of the actual time instant chosen for the lower limit of the integral, it is clear that we are making a kind of Markovian postulate. The consequence of this postulate is that the after-effect function $k(t)$ must be proportional to the autocorrelation function of the force, a theorem called the second fluctuation–dissipation theorem by Kubo (1966). It is then straightforward to show that

the velocity autocorrelation function is a mixture of two exponentials. Thus, let us assume that $V(t)$ obeys both (1) and (2)

$$\left.\begin{aligned} &\frac{\mathrm{d}V(t)}{\mathrm{d}t}+\int_0^t V(s)k(t-s)\,\mathrm{d}s = F(t) \\ &V(0) \textit{ independent of } F(t) \end{aligned}\right\} \tag{1}$$

$$\frac{\mathrm{d}V(t)}{\mathrm{d}t}+\int_{-\infty}^t V(s)k(t-s)\,\mathrm{d}s = F(t) \tag{2}$$

and let us further assume that $F(t)$ obeys the simple Langevin equation (3)

$$\frac{\mathrm{d}F(t)}{\mathrm{d}t}+\beta F(t) = E(t). \tag{3}$$

By substituting the expression for $F(t)$ given by first (1) and then (2) into (3), we obtain expressions for $V(t)$ in terms of the stochastic force $E(t)$. For example, using (1) we obtain

$$\frac{\mathrm{d}^2V}{\mathrm{d}t^2}+k(0)V+\beta\frac{\mathrm{d}V}{\mathrm{d}t}+\int_0^t\left(\frac{\mathrm{d}k(t-s)}{\mathrm{d}t}+\beta k(t-s)\right)V(s)\,\mathrm{d}s = E(t)$$

and the expression derived using (2) is exactly this expression except that the lower limit in the convolution is $-\infty$. If we require that the convolution term vanishes, irrespective of the value of the lower limit, it is clear that the integrand must vanish and this will be true provided $k(t)$ satisfies the same relation as the autocorrelation function for the force, namely, is of the form $k(0)\exp(-\beta t)$. Clearly the argument can be generalized to deal with any linear relation for the force $F(t)$ in terms of an uncorrelated force $E(t)$. Roughly speaking if $F(t)$ has a correlation function $R(\tau)$ which satisfies the $(n-1)$th order linear differential equation (4), with constant coefficients, then the velocity will satisfy the nth order linear differential equation (5) with constants related to those in (4).

$$R^{(n-1)}+a_{n-2}R^{(n-2)}+\ldots+a_0R = 0 \tag{4}$$

$$V^{(n)}+b_{n-1}V^{(n-1)}+\ldots+b_0V = E(t). \tag{5}$$

Thus equations (1) and (2) give the same stochastic behaviour as (5) provided the memory function $k(t)$ is chosen to satisfy (4). However we can regard the velocity $V(t)$ from (5) as being a projection of an n-dimensional Gaussian–Markov process whose components are, say, $V(t)$ and its time derivatives up to the $(n-1)$th. Thus the stochastic description of $V(t)$ is completely given when we know the values of $V(t)$ and the appropriate derivatives at a given time. In a sense this contradicts the spirit of the generalizations (1) and (2) in which the velocity was supposed to depend on the whole past of $V(t)$. Now, by thinking of a Taylor series expansion for $V(t)$ in the neighbourhood of $t = 0$, a complete statement of the history of $V(t)$ would be contained in the specification of derivatives of $V(t)$ of arbitrarily high order, whereas by using only the first $(n-1)$ derivatives we imply that only the immediate past is relevant. So by including derivatives of sufficiently high order in (5) it will be possible to account for correlations in $V(t)$ lasting over long times and with fairly complex structure.

On the other hand, Sears (1969) has shown that adding more and more derivatives to the *left* side of (5) may not give much greater accuracy in representing either the

correlation function $R(t)$ or its Fourier transform the power spectrum $P(w)$. If we define $P(w)$ so that

$$R(t) = \int_{-\infty}^{\infty} P(w) \exp(-iwt)\, dw$$

it is easily seen that the behaviour of $R(t)$ *near the origin* $t = 0$ is described by giving the moments μ_m of the spectrum

$$R(0) = \int P(w)\, dw = \mu_0$$

$$iR'(0) = \int P(w) w\, dw = \mu_1$$

$$-R''(0) = \int P(w) w^2\, dw = \mu_2$$

... etc.

Now the continued fraction representation of Sears (1969) or Mori (1965) leads to an expression for $R(t)$ as a mixture of n exponentials chosen so that all moments μ_m are given correctly up to the $(2n-2)$th. Thus the expression for $P(w)$ in the nth long time approximation, as this is called, is a constant divided by a polynomial $Q(w)$ of order n in w^2, and this is exactly what is obtained for the spectrum $P(w)$ derived from (5). In fitting these expressions to the velocity autocorrelation function for liquid argon as calculated from the computer experiments of Rahman (1964), Sears found that increasing the order of the polynomial $Q(w)$ gave increasingly good agreement but the rate of convergence was rather slow. In this case, it is clear that the form of power spectrum is too restrictive giving increasingly good agreement *near the time origin* $t = 0$, but giving poor results for low frequencies and long time correlations. A more general form, capable of representing the Rahman data accurately with relatively few arbitrary constants, results from choosing the generalized Langevin equation (5*a*)

$$V^{(n)} + b_{n-1} V^{(n-1)} + \ldots + b_0 V = a_m E^{(m)} + a_{m-1} E^{(m-1)} + \ldots + E. \qquad (5a)$$

This gives a spectrum which is a ratio of two polynomials in w^2 of orders m and n respectively. Moments of orders up to $(2n-2m-2)$ can be made equal to those calculated from the observed spectrum, leaving m arbitrary constants to be adjusted to get the best fit. Equation (5*a*) arises naturally when a system of coupled equations is considered, for example the itinerant oscillator models of Sears (1965) and Damle *et al* (1968). In any case the moment-fitting method only guarantees that the spectrum $P(w)$ has its first $(2n-2)$ moments correct. All higher order moments are infinite and are likely to have infinite error, so it would seem natural to relax the moment rules (as was done by Damle *et al* (1968)) so as to obtain better overall fit, especially for long time correlations. Since we are here concerned with the close relationship between the Gaussian–Markov properties and the fluctuation–dissipation theorems, we will not discuss the merits of given approximations any further. The most general form for the correlation function of a Gaussian–Markov process of order n is given by (6) and we will illustrate the procedure by solving the Langevin equation (5).

The correlation function appropriate to (5) can be found in a variety of ways. One way is to find the spectrum which will be a rational function of w^2, where w is the frequency. By factorizing the spectrum and expressing it as a sum of partial fractions it

can be shown that the correlation function is a sum of exponentials. We will assume that $R(\tau) = \langle V(t)V(t+\tau)\rangle$ can be put in the form (or approximated by)

$$R(\tau) = \sum_{i=1}^{n} d_i \exp(\beta_i|\tau|). \tag{6}$$

The equation which $R(\tau)$ must satisfy is obtained by setting $t = t+\tau$ in (5), multiplying both sides by $V(t)$ and averaging. Then $R(\tau)$ satisfies (7)

$$R^{(n)} + b_{n-1}R^{(n-1)} + \ldots + b_0 R = 0 \tag{7}$$

where we have used the fact that $E(t+\tau)$ is uncorrelated so that $\langle V(t)E(t+\tau)\rangle \equiv 0$.

On substituting expression (6) for $R(\tau)$ in (7), we see that the equation will be satisfied for all τ only if *each* of the exponentials in (6) satisfies (7), and this means that each of the constants β_i is to be a solution of (8)

$$\beta^n + b_{n-1}\beta^{n-1} + \ldots + b_0 = 0. \tag{8}$$

This equation will have n roots, in general complex, and we will assume these are all different. The constants d_i in (6) can be chosen, for example, to satisfy the requirement of stationarity that $R(\tau)$ should have odd derivatives equal to zero when $\tau = 0$, as well as satisfying the equipartition of energy result

$$R(0) = kT.$$

For example, let us take $n = 2$ in (6) so that

$$V^{(2)} + b_1 V^{(1)} + b_0 V = E(t).$$

Then there are two exponentials in the autocorrelation function for $V(t)$; with

$$\beta_i = \frac{-b_1 \pm (\sqrt{b_1^2 - 4b_0})^{1/2}}{2}$$

we get

$$R(\tau) = kT\{d_1 \exp(\beta_1\tau) + d_2 \exp(\beta_2\tau)\}.$$

Then the two conditions $R(0) = kT$ and $R'(0) = 0$ give

$$d_1 + d_2 = 1$$
$$\beta_1 d_1 + \beta_2 d_2 = 0$$

from which d_1 and d_2 can be determined. The solution is given in full detail by Ming Chen Wang and Uhlenbeck (1945) who give not only the correlations for $V(t)$, $\dot{V}(t)$ but give the complete derivation of all conditional averages for this system. These authors also use the Fokker–Planck equation to derive the averages. In our treatment we can derive, say, the autocorrelation function for $\dot{V}(t)$ by noting that

$$\begin{aligned}\langle \dot{V}(t)\dot{V}(t+\tau)\rangle &= -\langle V(t)\ddot{V}(t+\tau)\rangle \\ &= -R^{(2)}(\tau).\end{aligned}$$

Having obtained the formula (6) for $R(\tau)$, it is a simple matter to obtain a formal description of $V(t)$ in terms of an n-dimensional Markov process. Let us use orthogonal

coordinates for the Markov process, in the sense that n variables $Z_i(t)$ are chosen to form n independent Gaussian–Markov processes each satisfying

$$\langle Z_i(t)Z_i(t+\tau)\rangle = \exp(\beta_i|\tau|).$$

Then the projection $V(t)$ is a linear combination of the $Z_i(t)$, namely

$$V(t) = \sum_i c_i Z_i(t)$$

so that

$$\langle V(t)V(t+\tau)\rangle = \sum_i c_i^2 \exp(\beta_i|\tau|).$$

In view of the relations to be satisfied by the constants $d_i = c_i^2$, it is clear that the c_i may be imaginary in general.

4. Molecular motion in liquids

The molecular dynamics calculations of Rahman (1964) give an ideal opportunity for testing models of molecular motion. In applying these models however we should bear in mind two important results of Rahman's work, namely, that the velocities of the particles at a given time are distributed according to the Gaussian distribution, and that the distribution of the displacements $r(t)-r(0)$ is *not* Gaussian for small times t. Now the latter result shows that the velocity of a molecule is *not* a Gaussian process whereas the former result, together with the ergodic hypothesis, shows that the one-point distribution of velocity is Gaussian. In other words, although the *joint* distribution of $V(t_1)$ and $V(t_2)$ is *not* Gaussian, the one-point distribution of $V(t_1)$ is Gaussian.

Suppose $V(t)$ were Gaussian, that is, all n-point distributions are n-dimensional Gaussian, then

$$r(t)-r(0) = \int_0^t V(s)\,\mathrm{d}s$$

is also a Gaussian process since it is linearly related to $V(t)$. However we have already said that $r(t)-r(0)$ is not Gaussian so that $V(t)$ cannot be Gaussian to all orders. On the other hand, for sufficiently long times t, $r(t)$ will approach Gaussianity by virtue of the central limit theorem, and the condition for this to hold is that the time t should be much greater than the correlation time of the velocity. In effect, this is the theorem that narrow band filtering of a stationary process results in a Gaussian process.

The application of the simple Langevin equation, or for that matter the generalizations discussed here, is contradictory unless we can relax the condition of Gaussianity. Unfortunately the central limit theorem can be applied to the solution of (6) since we are assuming $E(t)$ to be uncorrelated. Thus it is necessary to include nonlinear effects in the equation of motion, or introduce non-Gaussianity into the force $E(t)$ if the correlation time of $E(t)$ is comparable with that of $V(t)$, before we can get non-Gaussianity in $r(t)$. Indeed the nonlinearities in the equation of motion are responsible for energy transfer between spectral components at different frequencies, so that it is unlikely that a linear model will give the correct behaviour for either the spectral density or the probability distributions. Despite this there are some linear models with a high content of physically appealing ideas about molecular motion in liquids. The most notable of these are the Sears' (1965) itinerant oscillator model of liquids and developments from

this model (Damle *et al* 1968). In these models the coefficients appearing in the equations of motion are estimated from a knowledge of the pair correlation function $g(r)$ and the intermolecular potential (known for Rahman's (1964) computer experiment). However the correlation function for the force is not known and is chosen to be exponential (Sears or Damle) or of the form $\exp(-\beta t^2)$ (Damle). The choice of a particular form is made for computational convenience and has no physical significance. However, as we have seen, an exponential form leads to an interpretation as a projection of a Markov process and this fits naturally into normal Brownian motion theory. On the other hand it is not clear if we can interpret the process with correlation function $\exp(-\beta t^2)$ as being Markov, since this would require a description of the velocity of the particle together with *all* its time derivatives.

We can state the problem in a slightly more concrete fashion. When dealing with the motion of a molecule it is impossible to take into account all coordinates of all N molecules and we try to describe the motion by a small subsystem with a few degrees of freedom, this subsystem being immersed in a heat bath representing all other degrees of freedom. If only M degrees of freedom are required to describe our subsystem (or model) then the subsystem is an M-dimensional Markov process, and any one coordinate of the subsystem will be a projection. For example, a model due to Wyllie (1969 unpublished), describes molecular motion as follows. A molecule is attached to a cage formed of near neighbours by an elastic force plus a damping term. The cage, supposed solid with mass $M \gg$ mass m of a molecule, is undergoing Brownian motion in the usual way. Assuming isotropy, the motion is thus a three-dimensional Gaussian–Markov process, and from fitting the resulting formulae to Rahman's data, it is possible to estimate the physical parameters used. Unfortunately these models tend not to be consistent since they predict an effective cage mass *less* than the molecular mass (eg Damle *et al* 1968).

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