# The generalized Langevin equation and the fluctuation- dissipation theorems



1971 J. Phys. A: Gen. Phys. 4 685

(http://iopscience.iop.org/0022-3689/4/5/011)

J. Phys. A: Gen. Phys., 1971, Vol. 4. Printed in Great Britain

# The generalized Langevin equation and the fluctuation–dissipation theorems

R. J. HENERY

Department of Mathematics, University of Strathclyde, Glasgow C1, Scotland

*MS. received* 11*th March* 1971

**Abstract.** Two forms of Langevin equation are used to describe the equilibrium and nonequilibrium behaviour of a particle undergoing a Brownian motion. By comparing the results of these two forms it is shown that the fluctuation–dissipation theorems depend on two main assumptions. First, the after-effect functions are the same for the equilibrium and nonequilibrium states and second, the velocity power spectra are identical or the velocity autocorrelation function $\langle V(t)V(t+T)\rangle$ does not depend on the time $t$ in the nonequilibrium state.

## 1. Introduction

Recently there have been several attempts at setting up models to describe molecular motion in liquids by means of a generalized Langevin equation. Not only do these models base themselves on physically reasonable descriptions of liquids, but the form of the Langevin equation is such as to allow us to use the fluctuation–dissipation theorems developed by Kubo (1957). These theorems have been developed from statistical mechanical arguments but Kubo (1966) and Damle *et al.* (1968) have given proofs which start from a generalized Langevin equation. Our purpose is to discuss the assumptions underlying these proofs; we do not deal with the validity of the fluctuation–dissipation theorems as such.

Since there are many assumptions involved, we proceed as gradually as possible, introducing assumptions only when necessary. Thus, in § 2 we start by solving the generalized Langevin equation (6) which represents a system which has been in motion for an infinite time and is in thermal equilibrium. From this we derive a formula relating the velocity power spectrum $G(w)$ to the spectrum of the random force, and a formula giving the mobility $\mu(w)$ in terms of the after-effect function $k(t)$: equations (13) and (19) respectively. These formulae describe the behaviour of a molecule in a stationary state.

In § 3, we solve the Langevin equation (7) for a molecule which was originally at rest for all instants before $t = 0$, and which is then given a velocity $V_0(0)$ chosen at random. The force $F(t)$ is assumed to develop independently of $V_0(0)$ in the sense:

$$\langle V_0(0)F(t)\rangle = 0 \qquad \text{Assumption I.}$$

In solving (7), we need no information as to how $F(t)$ develops immediately after $t = 0$ apart from this and the requirement of stationarity as $t$ tends to infinity. As might be expected, however, there are transients in the solution to (7) so that at least one of $V_0(t)$ and $F(t)$ is nonstationary. Since we need only the correlation function $\langle V_0(0)V_0(t)\rangle$ which describes the decay of the initial velocity $V_0(0)$, we will solve (7) for this quantity only. The Fourier transform of $\langle V_0(0)V_0(t)\rangle$ gives a second expression for the velocity power spectrum $G_0(w)$.

With two expressions for the velocity spectrum, we need extra assumptions to proceed further. In § 4 we assume that the after-effect functions appearing in (6) and (7) are the same, that is:

$$k_0(t) = k(t) \qquad \text{Assumption II.}$$

This leads to a form of the first fluctuation–dissipation theorem—to be referred to as FD1. Then we assume that the velocity spectrum for the stationary state $G(w)$ is the same as the velocity spectrum $G_0(w)$ which describes the nonstationary solution to (7):

$$G_0(w) = G(w) \qquad \text{Assumption III.}$$

By this means we may hope that (7) represents a situation which is not too far from equilibrium. Finally, we investigate how far the solution to (7) may be taken to be stationary.

## 2. Stationary Langevin

The simple phenomenological Langevin equation (1) is successful in describing random walks or diffusion processes, especially in the low frequency region:

$$\frac{dV}{dt}(t) + kV(t) = F(t). \tag{1}$$

Here the total force on the particle is $F(t) - kV(t)$ and the Langevin equation will be successful when the total force can be resolved into two components, $-kV(t)$ being that part of the total force which is correlated with the velocity $V(t)$, and $F(t)$ being the remainder. To solve (1), we assume that $F(t)$ is completely random in the sense:

$$\langle F(t)F(t+T) \rangle = 0 \qquad T > 0$$

and

$$\langle F(t)^2 \rangle = F^2. \tag{2}$$

Since the velocity depends only on past values of the force, and since past and future forces are uncorrelated, conditions (2) lead to equation (3):

$$\langle V(t)F(t+T) \rangle = 0 \qquad T > 0. \tag{3}$$

From this we see that assumption I is satisfied at all times when, and only when, the random force is white. Appropriate use of (3) simplifies the derivation of the autocorrelation function for the velocity. Thus, setting $t = t+T$ in equation (1), multiplying throughout by $V(t)$, and averaging over a canonical ensemble, we obtain

$$\frac{d}{dT}\langle V(t)V(t+T) \rangle = -k\langle V(t)V(t+T) \rangle$$

and we have replaced the differentiation with respect to $t$ by that with respect to $T$. The velocity autocorrelation function is now given by equation (4):

$$R(T) = \langle V(t)V(t+T) \rangle = \langle V_0(0)^2 \rangle \exp(-kT). \tag{4}$$

As is well known, this form of autocorrelation function is consistent only if the random force satisfies (3); that is, if it has a white spectrum. However, although formula (4) is useful for long times and low frequencies, it cannot represent the short-time behaviour of physical systems because $R(T)$ is even and should have a

Taylor series expansion in even powers of time $T$, whereas that given by (4) is

$$R(T) = V(0)^2 - a|T| + \dots$$

and this has discontinuous slope at $T = 0$.

The motives behind the proposed generalizations of the Langevin equation are two: (i) it is required to take account of forces which are correlated from one instant to the next thus broadening conditions (2); (ii) the viscous drag is to have a measure of inbuilt delay between the attainment of velocity $V$ and the resulting reaction. The physical reasoning for a particle in a liquid might be as follows:

*Motive* (i). The total force on a particle is dominated by the contribution from near neighbours, but we can separate out that part which is correlated with the velocity and call the remainder the 'random' component. Thus, the total force, $E(t)$, would be given by

$$E(t) = -kV + F(t). \tag{5}$$

As in elementary statistics, $-k = \langle V(t)E(t)\rangle / \langle V(t)^2 \rangle$ and the random part $F(t)$ is uncorrelated with $V(t)$. However, in a real liquid, the neighbouring particles change configuration in a time of order $\tau$ (say), so that $F(t) \simeq F(t + \mathrm{d}t)$ if $\mathrm{d}t$ is less than $\tau$. More generally, we assume that

$$\langle F(t)F(t+T)\rangle = R_{\mathrm{F}}(T)$$

where $R_{\mathrm{F}}(T)$ is the force autocorrelation function, assumed to be independent of time $t$, so that the force $F(t)$ is a stationary process.

*Motive* (ii). If the total force $E(t)$ is given by (5), we can say that the original cause for the velocity $V(t)$ is that the configuration of neighbours is such as to accelerate the particle in the given direction, and this configuration will last for a time of order $\tau$. Alternatively, if the neighbours are at rest and the particle is moving at velocity $V$, the neighbours will move in such a way as to reduce the total force and there will be a time delay (of the order of $\tau$) before this happens. Thus, over and above the correlation with the velocity at time $t$, the total force is partly correlated with the velocity at all previous moments.

Thus the generalization given by (6) is deemed to be physically reasonable and capable of describing correlated motions, as in liquids. In equation (6), the viscous drag is delayed—this is represented by the after-effect function $k(t)$ which gives the viscous drag at a time $t$ after a unit impulse velocity has been applied at $t = 0$. This after-effect function may very well depend on the initial conditions and on whether conditions are stationary or not. The force $F(t)$ is assumed to be nonwhite and independent of the initial conditions:

$$\dot{V}(t) + \int_{-\infty}^{t} k(t-s)V(s)\,\mathrm{d}s = F(t). \tag{6}$$

We will also consider the generalization given by (7) in which the after-effect function $k_0(t)$ differs from $k(t)$ in general

$$\dot{V}_0(t) + \int_{0}^{t} k_0(t-s)V_0(s)\,\mathrm{d}s = F_0(t). \tag{7}$$

In this way, by considering two forms for $k(t)$, we may go some way towards the more general form $k(t, s)$. In § 4, we will see what follows if assumption II is true, that is, if $k_0(t) = k(t)$. Both after-effect functions are assumed real; that is, they vanish for negative time.

So far the argument has followed that of Kubo (1966), but whereas he assumes the solution to (7) is stationary and derives thereafter the fluctuation theorems, we adopt a more cautious approach. The remainder of this section is devoted to solving (6) which may safely be taken to represent the stationary state. Using the method of Rice, it is possible to solve (6) and obtain all relevant correlation functions in terms of the properties of $k(t)$ and $F(t)$. We defer, until § 3, the consideration of (7), which we solve by a special device; since (7) is essentially nonstationary the Rice method is inappropriate.

The random force $F(t)$ is described by the formal representation given in (8) and (9):

$$F(t) = \int_{-\infty}^{\infty} (a(w)\cos(wt) + b(w)\sin(wt))\,dw \tag{8}$$

where

$$\begin{aligned} \langle a(w)a(w')\rangle = \langle b(w)b(w')\rangle &= S(w)\delta(w-w') \\ \langle a(w)b(w')\rangle &= 0 \qquad \text{for all } w, w'. \end{aligned} \tag{9}$$

$S(w)$ is the power spectrum of the process $F(t)$, $\delta(w)$ is the Dirac delta function. Thus, using these definitions,

$$\langle F(t)^2\rangle = \int_{-\infty}^{\infty} S(w)\,dw \qquad \text{(independent of } t\text{)}$$

and this relation is the reason for calling $S(w)$ the power spectrum. The velocity $V(t)$ will have a similar representation given by (10):

$$V(t) = \int_{-\infty}^{\infty} (c(w)\cos(wt) + d(w)\sin(wt))\,dw. \tag{10}$$

Inserting (8) and (10) in (6), we get the following expressions for $c(w)$ and $d(w)$ which constitute the required solution:

$$\begin{aligned} c(w) &= \frac{\{a(w)P(w) - b(w)(w - Q(w))\}}{Z(w)^2} \\ d(w) &= \frac{\{a(w)(w - Q(w)) + b(w)P(w)\}}{Z(w)^2} \end{aligned} \tag{11}$$

where we have written

$$P(w) = \int_0^{\infty} k(s)\cos(ws)\,ds$$

$$Q(w) = \int_0^{\infty} k(s)\sin(ws)\,ds$$

and

$$Z(w)^2 = P(w)^2 + (w - Q(w))^2.$$

It is easily verified that the $c(w)$ and $d(w)$ satisfy relations analogous to (9):

$$\begin{aligned} \langle c(w)c(w')\rangle = \langle d(w)d(w')\rangle &= G(w)\delta(w-w') \\ \langle c(w)\,d(w')\rangle &= 0 \qquad \text{for all } w, w' \end{aligned} \tag{12}$$

with the velocity power spectrum $G(w)$ given by

$$G(w) = \frac{S(w)}{Z(w)^2}. \tag{13}$$

We have now all the information necessary for evaluating all averages involving $F(t)$ and $V(t)$ or their time derivatives and it is a simple matter to demonstrate that these averages are all time-independent so that the process $V(t)$ is also stationary.

Before stating some correlation functions which we will require later, we will convert our results to complex notation. Equations (8) and (10) become (14) and (15) respectively, with the convention that only the real parts be taken:

$$F(t) = \int_{-\infty}^{\infty} F(\mathrm{i}w) \exp(-\mathrm{i}wt)\, \mathrm{d}w \tag{14}$$

$$V(t) = \int_{-\infty}^{\infty} V(\mathrm{i}w) \exp(-\mathrm{i}wt)\, \mathrm{d}w \tag{15}$$

where

$$F(\mathrm{i}w) = a(w) + \mathrm{i}b(w)$$

and

$$V(\mathrm{i}w) = c(w) + \mathrm{i}d(w).$$

By the substitution $\mathrm{i} = -\mathrm{i}$, we obtain the definitions for $F(-\mathrm{i}w)$ and $V(-\mathrm{i}w)$. The results expressed in (11) take the more concise form:

$$V(\mathrm{i}w) = \frac{F(\mathrm{i}w)}{Z(\mathrm{i}w)}$$

with

$$Z(\mathrm{i}w) = -\mathrm{i}w + k(\mathrm{i}w) = P(w) + \mathrm{i}\{Q(w) - w\}.$$

The power spectra for the force $F(t)$ and velocity $V(t)$ are now given by

$$S(w) = \langle F(\mathrm{i}w) F(-\mathrm{i}w) \rangle$$

and

$$G(w) = \langle V(\mathrm{i}w) V(-\mathrm{i}w) \rangle$$

$$= \frac{\langle F(\mathrm{i}w) F(-\mathrm{i}w) \rangle}{Z(\mathrm{i}w) Z(-\mathrm{i}w)} = \frac{S(w)}{Z(w)^2}$$

as before. In general, averages involving $V(t)$ and $F(t)$ may be evaluated using the definitions (14) and (15) and it will be found that these averages are time-independent. Therefore, to obtain the correlation function between two variables, say $V(t)$ and $F(t+T)$, we set $t = 0$ in (15) and $t = T$ in (14), then multiply the integrands and integrate over $w$:

$$\langle V(t) F(t+T) \rangle = \langle V(0) F(T) \rangle$$

$$= \int_{-\infty}^{\infty} \langle V(-\mathrm{i}w) F(\mathrm{i}w) \rangle \exp(-\mathrm{i}wT)\, \mathrm{d}w$$

$$= \int_{-\infty}^{\infty} \frac{S(w)}{\mathrm{i}w + k(-\mathrm{i}w)} \exp(-\mathrm{i}wT)\, \mathrm{d}w.$$

Since the real part is to be taken

$$\langle V(t)F(t+T)\rangle = \int_{-\infty}^{\infty} \frac{S(w)}{Z(w)^2}\{P(w)\cos(wT)-(w-Q(w))\sin(wT)\}\,dw. \tag{16}$$

This correlation function is the quantity which is assumed zero under assumption I, and although this is possible for some values of $T$ in the stationary state, it is not possible for all values of $T$. This is because the vanishing of (16) requires an even function of $T$ to be equal to an odd function of $T$. However, by admitting such unphysical correlation functions as that given in (4), we get a formal solution which will make $\alpha$ true. Kubo (1966) rejects such solutions for the very good reason that they contradict the assumption of stationarity by which all averages are assumed to be time independent. Thus, for the case discussed by Kubo, namely the average of $V(t)^2$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle V(t)^2\rangle = \langle 2V(t)\dot{V}(t)\rangle = 0$$

which contradicts the Taylor series expansion of $\langle V(t)V(t+T)\rangle$ given by (4).

We now state the formulae for several correlation functions which we require later. In deriving these, use may be made of the fact that the time derivatives of these functions vanish provided we do not use pathological functions such as (4) in trying to satisfy I:

$$R_1(T) = \langle V(t)V(t+T)\rangle = \int_{-\infty}^{\infty} \frac{S(w)}{Z(w)^2}\cos(wT)\,dw \tag{17}$$

$$R_2(T) = \langle \dot{V}(t)\dot{V}(t+T)\rangle = \int_{-\infty}^{\infty} \frac{S(w)}{Z(w)^2}w^2\cos(wT)\,dw \tag{18}$$

$$R_3(T) = \langle \ddot{V}(t)\ddot{V}(t+T)\rangle = \int_{-\infty}^{\infty} \frac{S(w)}{Z(w)^2}w^4\cos(wT)\,dw. \tag{19}$$

## 2.1. *Mobility*

If the driving force $F_0\cos(wt)$ is added to the random force $F(t)$ in (6), we can find the average steady state response $\langle V(t)\rangle$ by assuming that transients have decayed to zero so that $\langle V(t)\rangle$ is oscillating at the frequency $w$. Setting $\langle V(t)\rangle$ equal to the real part of $V(iw)\exp(iwt)$, we take the average of (6):

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle V(t)\rangle + \int_{-\infty}^{t}\langle V(s)\rangle k(t-s)\,\mathrm{d}s = F_0\cos(wt)$$

or

$$iwV(-iw)+V(-iw)k(-iw) = F_0$$

so that

$$V(-iw) = \frac{F_0}{iw+k(-iw)}$$

or

$$V(t) = \mathrm{Re}\{\mu(w)F_0\exp(iwt)\}$$

where we have written

$$\mu(w) = \frac{1}{iw+k(-iw)}. \tag{20}$$

The mobility $\mu(w)$ is only defined for the stationary state and should therefore be used for (6) or, in the long time limit, for (7). Thus, in deriving the corresponding quantity for (7), we must again assume that the transients have decayed to zero, so that we must effectively replace (7) by (6) and the mobility will then be given by (20) again.

## 3. Solution to (7)

The solutions to (6) and (7) should agree for times $t$ much greater than the decay time $\tau$ of the transients. For example, the correlation functions (17), (18) and (19) will give the long-time or steady-state behaviour so that only the short-time behaviour of (7) is of interest.

We emphasize that (7) contains transients which imply that (7) relates to a non-stationary state. To insist that $V(t)$ be stationary in the absolute sense would contradict the spirit of the generalizations (6) and (7) which were supposed to deal with different physical situations. In the extreme case that *both* (6) and (7) describe the equilibrium state, we see that the force $F_0(t)$ differs from $F(t)$ by a term $\int_{-\infty}^{0} k(t-s)V(s)\,\mathrm{d}s$ and of course (7) will give no information in addition to that which we have extracted from (6). By imposing suitable conditions, however, we may hope to make $V_0(t)$ partly stationary in that *some* correlation functions are independent of time. Thus, if we demand that the 'projection' of $V_0(T)$ on the original velocity be equal to the corresponding quantity in equilibrium, we have a kind of guarantee that $V_0(t)$ will remain close to thermal equilibrium. Indeed, this condition leads to a form of the fluctuation–dissipation theorem FD1.

Since complete knowledge of the short-time solution is not required, we project equation (7) on to the initial velocity $V_0(0)$ which is assumed to have been chosen at random from a canonical ensemble. We define the velocity $V_0(t)$ for instants prior to $t = 0$ to be identically zero.

Thus, multiplying (7) by $V_0(0)$ and averaging, and using assumption I since $V_0(0)$ is chosen independently of $F_0(0)$, we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle V_0(0)V_0(t)\rangle + \int_0^t \langle V_0(0)V_0(s)\rangle k_0(t-s)\,\mathrm{d}s = 0. \tag{21}$$

Taking the Fourier transform $\int_{-\infty}^{\infty}\exp(-\mathrm{i}wt)\,\mathrm{d}t$ of this last equation, we have

$$G_0(-\mathrm{i}w) = \frac{\langle V_0(0)^2\rangle}{\mathrm{i}w + k_0(-\mathrm{i}w)} \tag{22}$$

where

$$G_0(-\mathrm{i}w) = \int_0^\infty \langle V_0(0)V_0(t)\rangle \exp(-\mathrm{i}wt)\,\mathrm{d}t$$

and

$$k_0(-\mathrm{i}w) = \int_0^\infty k_0(t)\exp(-\mathrm{i}wt)\,\mathrm{d}t.$$

If we define the power spectrum $G_0(w)$ of $V_0(t)$ to be the real part of $G_0(-\mathrm{i}w)$, as is done by Kubo (1966), then $G_0(w)$ is given by (23):

$$G_0(w) = \mathrm{Re}\{G_0(-\mathrm{i}w)\} = \mathrm{Re}\left\{\langle V_0(0)^2\rangle \frac{1}{\mathrm{i}w + k_0(-\mathrm{i}w)}\right\}. \tag{23}$$

In order that the power spectrum in equilibrium be the same as the 'power spectrum' defined by the decay of the initial velocity, assumptions II and III must hold. In the next section we see what follows by assuming first II and then III.

A remarkable feature of (23) is that it has been derived without knowledge of the force $F_0(t)$—assumption I and the fact that we require only the correlation function $\langle V_0(t)V_0(0)\rangle$ have allowed us to do this. It is clear that $F_0(t)$ need not be wide sense stationary in order that (23) holds, and indeed on physical grounds we would expect $F(t)$ to be nonstationary. That either $F_0(t)$ or $V_0(t)$ is nonstationary may be shown quite simply by considering averages derived from (7) and comparing these with the corresponding averages derived from (6). Thus, for example, from (7) we have

$$\langle \dot{V}_0(0)^2\rangle = \langle F_0(0)^2\rangle$$

whereas from (18), representing the stationary result

$$\langle \dot{V}(t)^2\rangle = \int_{-\infty}^{\infty} \frac{w^2 S(w)\,\mathrm{d}w}{Z(w)^2}.$$

If we assume that $V_0(t)$ is stationary, we get the following equation for $\langle F_0(0)^2\rangle$:

$$\langle F_0(0)^2\rangle = \int_{-\infty}^{\infty} \frac{S(w)w^2\,\mathrm{d}w}{Z(w)^2}$$

whereas the definition of $S(w)$ gives:

$$\langle F(t)^2\rangle = \int_{-\infty}^{\infty} S(w)\,\mathrm{d}w$$

and these two expressions will give different values for the mean square force. Similarly, we can derive two expressions for $\langle \dot{F}(t)^2\rangle$, if this exists, one from the equilibrium state and from the initial value $\dot{F}_0(0) = \ddot{V}_0(0) - V_0(0)k_0(0)$ derived from (7). It will be seen that these give different answers if $V_0(t)$ is assumed stationary.

## 4. Fluctuation–dissipation theorems

The immediate consequence of taking II to be true is a form of the first fluctuation–dissipation theorem FD1. Comparing equations (20) and (22), we see that

$$\mu(w) = \frac{1}{\langle V_0(0)^2\rangle} G_0(-\mathrm{i}w)$$

or

$$\mu(w) = \frac{1}{\langle V_0(0)^2\rangle}\int_0^{\infty} \langle V_0(0)V_0(T)\rangle \exp(-\mathrm{i}wT)\,\mathrm{d}T \tag{24}$$

which is FD1, and which may also be referred to as the general admittance formula —it relates the (steady-state) transport coefficient $\mu(w)$ to the (transient) correlation function of flow $\langle V_0(0)V_0(T)\rangle$. In the original discussions of the FD theorems, $\mu(w)$ was given in terms of the fluctuations in equilibrium so that we would like to substitute the steady-state correlation function in (24), and, as already mentioned in § 3, this helps to ensure that $V_0(t)$ remains as close as possible to thermal equilibrium. Thus, making assumption III we obtain:

$$\mu(w) = \frac{1}{\langle V^2(t)\rangle}\int_0^{\infty} \langle V(t)V(t+T)\rangle \exp(-\mathrm{i}wT)\,\mathrm{d}T \tag{25}$$

which is the usual form of FD1. As a further benefit of assuming III, the second fluctuation–dissipation theorem FD2 follows. Writing (23) as

$$G_0(w) = \pi G(w) = \langle V(0)^2 \rangle \frac{\mathrm{Re}(k(-\mathrm{i}w))}{Z(w)^2}$$

and comparing this last equation with (13), we see that

$$\pi S(w) = \langle V(0)^2 \rangle \mathrm{Re}(k(-\mathrm{i}w)) \tag{26}$$

or

$$k(-\mathrm{i}w) = \frac{1}{\langle V(0)^2 \rangle} \int_0^\infty \langle F(t)F(t+T) \rangle \exp(-\mathrm{i}wT)\, \mathrm{d}T \tag{27}$$

and this is FD2, which we can state as effectively equating the after-effect function $k(t)$ with the correlation function of the random force. Thus both FD1 and FD2 depend on all three assumptions. If we were to avoid the assumptions and derived FD1 and FD2 from (6) alone, we would need the following generalization of I:

$$\langle V(t)F(t+T) \rangle = \int_{-\infty}^{t} \langle V(t)V(s) \rangle k(t+T-s)\, \mathrm{d}s.$$

With this condition, the velocity autocorrelation function satisfies (21) in equilibrium and FD1 and FD2 then relate to the equilibrium state alone.

## 5. Example

There is one case in which we can write down explicit solutions to (6) and (7). This case occurs when a stationary random force $F(t)$, of known spectral density, is applied to a system with an exponential decay function $k(t) = k \exp(-\alpha t)$. The solution to (6) is given by (10); and we can obtain the solution to (7) by considering the equation of motion for the difference $v(t)$:

$$v(t) = V_0(t) - V(t)$$

namely

$$\dot{v}(t) + \int_0^t kv(s) \exp\{-\alpha(t-s)\}\, \mathrm{d}s = \exp(-\alpha t)\{F(0) - \dot{V}(0)\} \tag{28}$$

the result for $V_0(t)$ is

$$V_0(t) = V(t) + A \exp(-\alpha_1 t) + B \exp(-\alpha_2 t) \tag{29}$$

where

$$2\alpha_1 = \alpha + (\alpha^2 - 4k)^{1/2}$$

$$2\alpha_2 = \alpha - (\alpha^2 - 4k)^{1/2}$$

and $A$, $B$ are constants depending linearly on the initial values of $V(t)$, $\dot{V}(t)$, $V_0(t)$ and $F(t)$. Note that $V_0(t) \to V(t)$ as $t \to \infty$ so that the terms containing $A$ and $B$ are transients.

For example, multiply (29) by $V_0(0)$ and average giving

$$\langle V_0(0)V_0(t) \rangle = \langle AV_0(0) \rangle \exp(-\alpha_1 t) + \langle BV_0(0) \rangle \exp(-\alpha_2 t)$$

$$= \frac{\langle V_0(0)^2 \rangle}{(\alpha \quad \alpha_2)} \{\alpha_1 \exp(-\alpha_2 t) - \alpha_2 \exp(-\alpha_1 t)\}. \tag{30}$$

Obviously (30) describes the average transient behaviour, but if we make the equilibrium autocorrelation function $\langle V(t)V(t+T)\rangle$ equal to the expression on the right of (30), then we can expect that $V_0(t)$ will not be far removed from stationarity. Thus, in the Taylor series:

$$\langle V_0(t)^2\rangle = \langle V_0(0)^2\rangle + t\frac{\mathrm{d}}{\mathrm{d}t}\langle V_0(0)^2\rangle + \ldots$$

all coefficients of $t$, $t^2$, etc. should vanish.

The first two coefficients, those of $t$ and $t^2$ are respectively

$$\langle V_0(0)F(0)\rangle$$

and

$$\langle F(0)^2 - kV_0(0)^2\rangle$$

and it will be seen that these vanish under assumptions I and III. However, the coefficient of $t^3$ is not zero in general, and $V_0(t)$ is therefore not stationary. The departure from stationarity is relatively small since for small times the $t^3$ term will be small and for times of order $\alpha_2^{-1}$ the transient terms are decaying fast.

## References

DAMLE, P. S., SJOLANDER, A., and SINGWI, K. S., 1968, *Phys. Rev.*, **165**, 277–82.
KUBO, R., 1957, *J. Phys. Soc. Japan*, **21**, 570–86.
—— 1966, in *Many Body Theory*, ed. R. Kubo (Tokyo: Syokabo and Benjamin).