Simple derivations of generalized linear and nonlinear Langevin equations

1973 J. Phys. A: Math. Nucl. Gen. 6 1289

(http://iopscience.iop.org/0301-0015/6/9/004)

J. Phys. A: Math., Nucl. Gen., Vol. 6, September 1973. Printed in Great Britain.

Simple derivations of generalized linear and nonlinear Langevin equations

Kyozi Kawasaki†

Department of Physics, Temple University, Philadelphia, Pennsylvania 19122, USA

Received 19 March 1973

Abstract. With the aid of a single operator identity, the derivation of the Mori generalized linear Langevin equation is simplified and a new generalized nonlinear Langevin equation is obtained. The flexibility of the method is stressed which allows us to derive various generalized nonlinear Langevin equations that can be used as bases for devising approximation schemes such as the mode coupling scheme.

1. Introduction

In recent years formally exact generalized Langevin equations (Mori 1965, Kubo 1966) are proving to provide useful starting points in various problems of non-equilibrium statistical mechanics. Notable examples are the memory function approaches to liquid dynamics (Akcasu and Duderstadt 1969, Mazenko 1971) and the study of non-equilibrium critical phenomena (Kawasaki 1972). In view of the importance of these generalized Langevin equations it is useful to simplify and generalize derivations of these equations. We accomplish this with the aid of an operator identity (2.2) below. The merits of our approach are its simplicity and greater flexibility. We first derive the generic Langevin equation (2.9), from which both linear and nonlinear generalized Langevin equations of various types are readily obtained by the suitable choice of projection operators (see §§ 3 and 4). Fluctuations from a non-equilibrium steady state are also treated in § 5.

2. Generic form of Langevin equation

In this section we present a derivation of the Langevin equation in a rather general form emphasizing its essential mathematical structure. Consider a (classical or quantum-mechanical) dynamical variable X_t whose time development can be described by a classical or quantum-mechanical Liouville operator $\mathscr{L}$ by‡

$$X_t = \mathrm{e}^{\mathrm{i}t\mathscr{L}}X \tag{2.1}$$

where X is equal to X_t at $t = 0$. We need another operator $\mathscr{L}_0$ which will be specified

† Now at Research Institute for Fundamental Physics, Kyoto University, Kyoto 606, Japan.

‡ In fact in quantum-mechanical cases $\mathscr{L}$, $\mathscr{L}_0$ and $\mathscr{P}$ in this section are 'super operators' that map a quantum-mechanical operator into another quantum-mechanical operator.

later and is closely related to $\mathscr{L}$. The first step in our derivation is to note the following operator identity:

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{e}^{\mathrm{i}t\mathscr{L}} = \mathrm{e}^{\mathrm{i}t\mathscr{L}}\mathrm{i}\mathscr{L}_0 + \int_0^t \mathrm{d}s\, \mathrm{e}^{\mathrm{i}(t-s)\mathscr{L}}\mathrm{i}\mathscr{L}_0\, \mathrm{e}^{\mathrm{i}s(\mathscr{L}-\mathscr{L}_0)}\mathrm{i}(\mathscr{L}-\mathscr{L}_0) + \mathrm{e}^{\mathrm{i}t(\mathscr{L}-\mathscr{L}_0)}\mathrm{i}(\mathscr{L}-\mathscr{L}_0). \tag{2.2}$$

This identity is very easily obtained if we note that the integrand in the above expression is also written as

$$-\frac{\mathrm{d}}{\mathrm{d}s}\mathrm{e}^{\mathrm{i}(t-s)\mathscr{L}}\,\mathrm{e}^{\mathrm{i}s(\mathscr{L}-\mathscr{L}_0)}\mathrm{i}(\mathscr{L}-\mathscr{L}_0). \tag{2.3}$$

Note that this identity is different from other operator identities used in a similar context such as equation (3.8) of Fukui and Morita (1971).

Let us now suppose that there is an inner product (X, Y) of two arbitrary dynamical variables X and Y. In this section we do not need a precise definition of such inner products although these will be explicitly defined in the examples later.

Physically speaking, a generalized Langevin equation expresses the fact that a macroscopic system exhibits slowly varying gross behaviour described by a set of gross variables $A_1, A_2, \ldots$ superimposed with rapid random fluctuating motions (Green 1952, Mori 1965, Kubo 1966). An arbitrary dynamical variable X is then separated into a part that is associated with the gross variables $\{A\}$ and the rest†. This we accomplish with the aid of the two sets of suitably defined functions of $\{A\}$, $\phi_n(\{A\})$ and $\psi_n(\{A\}), n = 1, 2, \ldots$, which are orthonormal in the following sense:

$$(\phi_m, \psi_n) = \delta_{mn}. \tag{2.4}$$

We then introduce the projection operator $\mathscr{P}$ by

$$\mathscr{P}X = \sum_n (X, \psi_n)\phi_n(\{A\}), \tag{2.5}$$

The condition (2.4) then ensures the idempotent nature of $\mathscr{P}$. The aforementioned separation of X is then

$$X = \mathscr{P}X + \mathscr{Q}X \tag{2.6}$$

with $\mathscr{Q} \equiv 1 - \mathscr{P}$ where $\mathscr{Q}X$ represents the rapid randomly fluctuating part of X. The choice of gross variables has been discussed (eg Green 1952) and will not be touched here. The choice of the orthonormal sets of functions $\{\phi_n\}$ and $\{\psi_n\}$ remains unspecified in this section. In particular we do not necessarily require these sets to be complete in the function space of $\{A\}$. The choice is dictated in each circumstance by what we want to regard as random forces. We also introduce the adjoints to $\mathscr{L}$ and $\mathscr{P}$ denoted by $\tilde{\mathscr{L}}$ and $\tilde{\mathscr{P}}$ as follows:

$$(\mathrm{i}\mathscr{L}X, Y) = -(X, \mathrm{i}\tilde{\mathscr{L}}Y) \tag{2.7}$$

$$(\mathscr{P}X, Y) = (X, \tilde{\mathscr{P}}Y) \tag{2.8}$$

where X and Y are arbitrary dynamical variables.

† This is a rather loose statement. The precise meaning of this requires specification of a projection operator also. See the following sections.

We now choose $\mathscr{L}_0$ in (2.2) to be $\mathscr{P}\mathscr{L}$ and apply (2.2) to X_t with the following result:

$$\frac{\mathrm{d}}{\mathrm{d}t}X_t = \sum_n (\mathrm{i}\mathscr{L}X, \psi_n)\phi_n(\{A_t\}) - \sum_n \int_0^t (f_X(s), \tilde{f}_n)\phi_n(\{A_{t-s}\})\,\mathrm{d}s + f_X(t) \tag{2.9}$$

where

$$f_X(t) \equiv \mathrm{e}^{\mathrm{i}t(1-\mathscr{P})\mathscr{L}}\mathrm{i}(1-\mathscr{P})\mathscr{L}X \tag{2.10}$$

$$\tilde{f}_n \equiv (1-\tilde{\mathscr{P}})\mathrm{i}\tilde{\mathscr{L}}\psi_n(\{A\}). \tag{2.11}$$

Here the second term of (2.9) has been transformed using (2.2) and (2.8), and we have used the following property satisfied by the Liouville operator:

$$\mathscr{L}XY = (\mathscr{L}X)Y + X(\mathscr{L}Y). \tag{2.12}$$

The equation (2.9) is the prototype of the generalized Langevin equation. Here the first term on the right-hand side represents the change of X_t in time which follows adiabatically the changes in $\{A_t\}$. The second term expresses the damping of this adiabatic motion by friction which contains memory effects. The last term is the random force acting upon the dynamical variable X. Of course this interpretation is always contingent on a particular separation of dynamical variables (2.6), that is, on the particular choice of $\{A\}$, $\{\psi_n\}$ and $\{\phi_n\}$. Note that the random forces satisfy the following orthogonality conditions:

$$(f_X(t), \psi_n) = 0 \tag{2.13}$$

$$(\phi_m, \tilde{f}_n) = 0. \tag{2.14}$$

The random forces are not necessarily orthogonal to functions of $\{A\}$ which are outside the function space spanned by $\{\phi\}$ and $\{\psi\}$. This characterizes how 'random' in fact f_X and $\tilde{f}_n$ are.

3. Generalized linear Langevin equation

We now derive as a special case of (2.9) the generalized linear Langevin equation for the quantum-mechanical gross variable A_i first obtained by Mori (1965). Here we define the inner product to be the Kubo canonical correlation (Kubo 1966),

$$(X, Y) \equiv (\beta Z)^{-1}\,\mathrm{Tr}\int_0^\beta \mathrm{d}\lambda\,\mathrm{e}^{-(\beta-\lambda)H}X\,\mathrm{e}^{-\lambda H}Y^\dagger \tag{3.1}$$

where $\beta \equiv 1/k_\mathrm{B}T$, Z is the partition function, and H is the system hamiltonian. $\mathscr{L}$ is defined by

$$\mathrm{i}\mathscr{L}X = -\frac{\mathrm{i}}{\hbar}[X, H] \tag{3.2}$$

and is hence self-adjoint: $\tilde{\mathscr{L}} = \mathscr{L}$. We choose the set of gross variables $\{A\}$ to be orthogonal to each other,

$$(A_i, A_j) = \chi_i\delta_{ij} \tag{3.3}$$

and ϕ and ψ are chosen to be

$$\phi_i(\{A\}) \equiv \chi_i^{-1/2} A_i \tag{3.4}$$

$$\psi_i(\{A\}) \equiv \chi_i^{-1/2} A_i \tag{3.5}$$

where the equilibrium averages A_i are taken to be zero. $\mathscr{P}$ is then identical to the projection operator of Mori (1965). Hence, choosing X_t to be $A_i(t) \equiv e^{it\mathscr{L}} A_i$, (2.9) reduces to

$$\frac{d}{dt} A_i(t) = \sum_j i\omega_{ij} A_j(t) - \sum_j \int_0^t (f_i(s), f_j)\chi_j^{-1} A_j(t-s) + f_i(t) \tag{3.6}$$

where

$$i\omega_{ij} \equiv (i\mathscr{L} A_i, A_j)\chi_j^{-1} \tag{3.7}$$

$$f_i(t) \equiv e^{it(1-\mathscr{P})\mathscr{L}}(1-\mathscr{P}) i\mathscr{L} A_i. \tag{3.8}$$

(3.6) is equivalent to Mori's generalized Langevin equation (Mori 1965).

4. Generalized nonlinear Langevin equations

In the preceding section the random forces $\{f\}$ are orthogonal only to the linear function of the gross variables $\{A\}$. It is now increasingly realized that this is not always satisfactory since the random force can then contain products of the gross variables which may not be really random (eg Kawasaki 1971, 1972, Zwanzig 1972). Hence the opposite extreme is to include all the suitably symmetrized polynomials of $\{A\}$ among the sets $\{\psi\}$ and $\{\phi\}$†. Otherwise we use the same definitions of the Liouville operator and inner products as in the preceding section. We then find from (2.9) with $X_t = A_i(t)$ the exact generalized nonlinear Langevin equation where now the random forces are orthogonal to all the polynomials of $\{A\}$ and hence can be considered as genuinely random provided the set $\{A\}$ exhausts all the slowly varying dynamical variables of the system.

The generalized Langevin equation assumes a rather compact form if we restrict ourselves to classical-mechanical cases. Here we may choose

$$\psi_n(\{A\}) = \phi_n(\{A\}) \tag{4.1}$$

and we further require the completeness condition,

$$\sum_n \phi_n(\{A\})\phi_n^*(\{A'\}) = \delta(A-A')P_e^{-1}(\{A\}) \tag{4.2}$$

where asterisk denotes taking the complex conjugate, and $\delta(A-A')$ is the product of delta functions of all the gross variables and $P_e(\{A\})$ is the equilibrium distribution function of the gross variables. With this choice of orthogonal set $\mathscr{P}$ becomes identical to the projection operator introduced by Zwanzig (1960). (2.9) then becomes

$$\frac{d}{dt} A_i(t) = v_i(\{A(t)\}) + \sum_j \int_0^t ds P_e^{-1}(\{A(t-s)\}) \frac{\partial}{\partial A_j^*(t-s)} K_{ij}^0(s; \{A(t-s)\})$$
$$\times P_e(\{A(t-s)\}) + f_i(t) \tag{4.3}$$

† An example of such a set of polynomials is suggested by Zwanzig (1972).

where

$$v_i(\{a\}) \equiv \langle \mathrm{i}\mathscr{L} A_i ; \{a\} \rangle \tag{4.4}$$

$$K^0_{ij}(t ; \{a\}) \equiv \langle f_i(t) f^*_j(0) ; \{a\} \rangle \tag{4.5}$$

$$f_i(t) \equiv \mathrm{e}^{\mathrm{i}t(1-\mathscr{P})\mathscr{L}}(1-\mathscr{P})\mathrm{i}\mathscr{L} A_i \tag{4.6}$$

with

$$\langle X ; \{a\} \rangle \equiv \frac{\langle X \delta(A-a) \rangle_{\mathrm{e}}}{P_{\mathrm{e}}(\{a\})}, \tag{4.7}$$

$\langle \ldots \rangle_{\mathrm{e}}$ being the equilibrium average. In deriving (4.3) we have used (4.2) and

$$\tilde{f}_n \equiv (1-\mathscr{P})\mathrm{i}\mathscr{L}\phi_n(\{A\}) = \sum_i \frac{\partial \phi_n(\{A\})}{\partial A_i} f_i \tag{4.8}$$

which follows by noting that

$$\mathscr{P} X F(\{A\}) = F(\{A\}) \mathscr{P} X \tag{4.9}$$

where $F(\{A\})$ is an arbitrary function of $\{A\}$.

If $f_i(t)$ is genuinely random, we may use the 'markovian' approximation

$$K^0_{ij}(t ; \{a\}) \cong 2L^0_{ij}(\{a\})\delta(t) \tag{4.10}$$

and obtain

$$\frac{\mathrm{d}}{\mathrm{d}t} A_i(t) = v_i(\{A(t)\}) + P_{\mathrm{e}}^{-1}(\{A(t)\}) \sum_j \frac{\partial}{\partial A^*_j(t)} L^0_{ij}(\{A(t)\}) P_{\mathrm{e}}(\{A(t)\}) + f_i(t). \tag{4.11}$$

$v_i(\{A(t)\})$ in general contains products of $\{A(t)\}$, and (4.11) can be used as a starting point for developing the mode-coupling theory (Kawasaki 1972). The identity (4.3) thus provides a generalization of the equation like (4.11) which contains memory effects associated with the random force $f_i(t)$ in the form of the memory kernel $K^0_{ij}(t ; \{A(t)\})$. (4.3) is the new result obtained here† although similar equations in less transparent forms have appeared in the literature (Kawasaki 1970, Nordholm 1972).

5. Fluctuations from steady states

In the preceding two sections we were concerned with fluctuations occurring in thermal equilibrium states. Here we show that the formalism of § 2 is also suited to study fluctuations occurring in steady states. To be specific, let us consider, following McLennan (1963), a system described by classical mechanics which is in a steady state maintained by a set of non-conservative forces F_α acting on the αth canonical coordinate of the system.

The equation of motion of an arbitrary dynamical variable of the system X is then

$$\frac{\mathrm{d}}{\mathrm{d}t} X_t = \mathrm{i}\mathscr{L} X_t \equiv \mathrm{i}\mathscr{L}_s X_t + \sum_\alpha F_\alpha \frac{\partial X_t}{\partial p_\alpha} \tag{5.1}$$

where $\mathscr{L}_s$ is the Liouville operator of the system isolated from the surrounding reservoirs

† This result was announced without derivation at the Symposium on Synergetics, Schloss Elmau, Germany, May 1972.

and p_α is the momentum conjugate to the αth coordinate. F_α and p_α are taken to be real quantities.

The Liouville equation for the phase-space distribution function $D(x;t)$ for the system in contact with reservoirs is (x is the phase-space coordinate),

$$\frac{\partial}{\partial t}D(x;t) = -\mathrm{i}\hat{\mathscr{L}}D(x;t) \tag{5.2}$$

with

$$\mathrm{i}\hat{\mathscr{L}}X \equiv \mathrm{i}\mathscr{L}_s X + \sum_\alpha \frac{\partial}{\partial p_\alpha}(F_\alpha X). \tag{5.3}$$

The steady state distribution function $D_0(x)$ then satisfies the equation

$$\mathrm{i}\hat{\mathscr{L}}D_0(x) = 0. \tag{5.4}$$

The inner product of phase functions X and Y is defined as

$$(X, Y) \equiv \int X(x)Y^*(x)D_0(x)\,\mathrm{d}x. \tag{5.5}$$

Then one can readily verify that $\mathscr{L}$ and $\hat{\mathscr{L}}$ are both self-adjoint operators. Furthermore, $\mathscr{L}$ satisfies the property (2.12) though $\hat{\mathscr{L}}$ in general does not.

We can now choose $\psi_n = \phi_n$ so that $\mathscr{P}$ is self-adjoint. If the set of functions $\{\phi\}$ either consists of linear functions of $\{A\}$ as in (3.4) or constitutes the complete set in the sense of (4.2) where $P_e(\{A\})$ is replaced by its equivalent in the steady state, we have for $\tilde{f}_n$ defined by (2.11) the following:

$$\tilde{f}_n = \sum_i \frac{\partial \phi_n(\{A\})}{\partial A_i} f_i. \tag{5.6}$$

With these preparations we recover, for these two choices of the set $\{\phi\}$, the classical version of the Mori generalized linear Langevin equation (3.6) and the generalized nonlinear Langevin equation (4.3) for fluctuations from a steady state, where the Liouville operator and the inner product are redefined in this section and equilibrium averages are replaced by steady-state averages.

6. Concluding remarks

In the preceding three sections we considered the two extreme choices of the sets of orthogonal functions $\{\phi\}$ and $\{\psi\}$. One can of course consider the whole intermediate range of choices of $\{\phi\}$ and $\{\psi\}$. For instance, one could choose linear and quadratic functions of $\{A\}$ for $\{\phi\}$ and $\{\psi\}$, which then gives the starting stochastic equations of the mode-coupling theory in which only two mode intermediate states are allowed. Then the processes involving three, four,... mode intermediate states must come from random forces. The greater flexibility afforded by our approach should provide a basis for devising suitable approximations in various specific circumstances.

Acknowledgments

The National Science Foundation is thanked for its support of this work.

References

Akcasu A Z and Duderstadt J J 1969 *Phys. Rev.* **188** 479
Fukui Y and Morita T 1971 *J. Phys.* A: *Gen. Phys.* **4** 477
Green M S 1952 *J. chem. Phys.* **20** 1281
Kawasaki K 1970 *Ann. Phys., NY* **61** 1
—— 1971 *Rendiconti S. I. F., Course LI* ed M S Green (New York: Academic Press)
—— 1972 *Statistical Mechanics* ed S Rice, K Freed and J Light (Chicago: University of Chicago Press)
Kubo R 1966 *Rep. Prog. Phys.* **29** 255
McLennan J A 1963 *Advances in Chemical Physics* vol 5, ed I Prigogine (New York: Interscience)
Mazenko G F 1971 *Phys. Rev.* A **3** 2121
Mori H 1965 *Prog. theor. Phys.* **33** 423
Nordholm K S J 1972 *PhD Thesis* University of Maryland
Zwanzig R 1960 *J. chem. Phys.* **33** 1388
—— 1972 *Statistical Mechanics* ed S Rice, K Freed and J Light (Chicago: University of Chicago Press)