

On the Derivation of the Generalized Langevin Equation for Interacting Brownian Particles

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Received April 25, 1980

The main result of this paper is a derivation of a generalized nonlinear Langevin equation (GLE) for n interacting particles in a bath. A consequence of the derivation is that the exact form of the (generalized) fluctuation-dissipation theorem is obtained. We discuss also the relation between the memory kernel of the GLE and some corresponding correlation functions which can be easily obtained in a molecular dynamics computer experiment. In the same spirit it is shown that the approach applies to a Brownian particle subjected to a stationary external field. The technique presented in a previous paper to simulate generalized Brownian dynamics can be easily extended to the present case. Our derivation intends to clarify the uses and (possibly) abuses of the Langevin equation in Brownian dynamics studies.

KEY WORDS: Generalized Brownian motion of n particles; Mori projection technique; fluctuation-dissipation theorem; generalized Brownian dynamics computer experiments.

1. INTRODUCTION

The computer simulation of Brownian motion, named Brownian dynamics (BD) by Turq *et al.*,⁽¹⁾ has recently received great attention on the ground that it permits the study of the time evolution of a set of relevant variables providing a (simpler) stochastic description of the "heat bath" formed by all other degrees of freedom. A certain number of BD simulations have appeared in the literature to tackle, within this general philosophy, a large

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variety of physical problems.⁽¹⁻⁸⁾ Quite recently^(9,10) it has been conclusively shown that also the Brownian motion corresponding to a wide class of GLE, i.e., a Brownian motion with memory effects, can be integrated. Let us call it generalized Brownian dynamics (GBD) including BD as a special case.

The most interesting applications of GBD require a model where the Brownian particles interact via a given potential and/or are subjected to an external stationary field. A typical example is provided by a set of n particles in solution. The corresponding stochastic equations of motion are usually written as⁽¹¹⁾

$$\begin{aligned} \frac{dp_{i,\alpha}}{dt} = & - \int_0^t d\tau \sum_{j,\beta} \gamma_{\alpha,j\beta}(t-\tau) p_{j,\beta}(\tau) + R_{i,\alpha}(t) \\ & + \sum_{\substack{j \\ \neq i}} F_{\alpha}^{ij}(|\mathbf{r}_j(t) - \mathbf{r}_i(t)|) + F_{\alpha}^{\text{ext}}(\mathbf{r}_i(t)), \quad i, j = \overline{1, n}; \alpha, \beta = \overline{1, 3} \end{aligned} \quad (1.1)$$

where $\gamma_{\alpha,j\beta}(t)$ are the memory functions, $R_{i,\alpha}(t)$ is the so-called “random force” acting on the i th particle, $F_{\alpha}^{ij}(|\mathbf{r}_j - \mathbf{r}_i|)$ is the force on Brownian particle i due to the j th one, and $F_{\alpha}^{\text{ext}}(\mathbf{r}_i(t))$ is an external field. However, here is an important deficiency in this philosophy. In fact, the original derivation by Mori⁽¹²⁾ of the GLE does not contain the more general case (1.1) and, to our knowledge, no attempt has been made to fill this gap on a statistical mechanics basis. Any proof of (1.1) is still lacking. In a different context a family of strict Langevin equations for interacting Brownian particles has been obtained.⁽¹³⁻¹⁵⁾ However, these derivations are not useful here because they do not apply when memory effects are present. Moreover, the form of the fluctuation dissipation theorem in this case is far from clear. The aim of this work is not to exploit once more Eq. (1.1), but to give, following the Mori approach, an exact derivation of it. In doing so we will also obtain the relation between the kernel $\underline{\gamma}$ and the autocorrelation of the random force.

The structure of this work is as follows. In Section 2 we recall the main results of the Mori derivation and we apply it to a suitable (vectorial) dynamical variable which permits us to separate the effect of the medium from the interactions to be treated explicitly. The Mori GLE can then be transformed easily into Eq. (1.1) if a part of the convolution term is transferred into the random force term; in this way the analog of the second fluctuation-dissipation theorem is shown to be much more complex than it has been usually assumed.

In Section 3, we give the physical meaning of the memory kernel and we comment on the possibility of substituting bare interactions with solvent-mediated effective ones.

In Section 4 we give the essential steps needed to realize the computer simulation of this type of generalized Brownian motion.

In Section 5 we come to some conclusions, we comment on the limitations of Eq. (1.1), and we draw attention to the fact that to really exploit this approach some physical extension of our derivation is needed so as to exclude from the random part the effect of the Brownian particles' configurations and to maintain some clear physical meaning to the memory kernel.

2. THE DERIVATION OF EQUATION (1.1)

Our starting point is the central result of the Mori paper on Brownian motion.^(12a) Let us restate it.

Given a Hamiltonian system of N particles and a set of dynamical variables $\{X_i\}_{i=1,3n}$ associated with it such that the X_i (i) are stationary stochastic variables with zero average and (ii) have the same time-reversal parity, the time evolution of the vectorial process $X_i(t)$ can be described by a vectorial GLE of the form

$$\dot{X}_i(t) = - \sum_j \int_0^t \Gamma_{ij}(t - \tau) X_j(\tau) d\tau + R_i(t), \quad i = \overline{1, 3n} \quad (2.1)$$

with (denoting with \underline{X}^T and $\underline{\Gamma}^T$ the transposed vector or matrix, respectively)

$$\underline{R}(0) = \dot{\underline{X}}(0) \quad (2.2a)$$

$$\langle \underline{R}(t) \rangle = \underline{0} \quad (2.2b)$$

$$\langle \underline{R}(t) \underline{R}^T(t') \rangle = \underline{\Gamma}(t - t') \langle \underline{X} \underline{X}^T \rangle^{-1} \quad (2.2c)$$

$$\langle \underline{R}(t) \underline{X}^T(0) \rangle = \underline{0} \quad (2.2d)$$

$$\langle \underline{R}(t + t') \underline{X}^T(t') \rangle = \int_0^{t'} ds \langle \underline{R}(t + t') \underline{R}^T(t' - s) \rangle \langle \underline{X} \underline{X}^T \rangle^{-1} \langle \underline{X} \underline{X}^T(s) \rangle \quad (2.2e)$$

The derivation of Eq. (2.1) and properties (2.2) have been reviewed so many times (see, for example, Ref. 11) that we will not insist on it. Note, however, that properties (2.2) are valid by construction. In particular (2.2c) means that \underline{R} and \underline{X} are not stationarily correlated.

In order to illustrate our derivation in a definite way, let us consider the case of a set A of n particles in a bath B of $(N - n)$ solvent particles in the presence of an external stationary field. The Hamiltonian of this system

can be written

$$\begin{aligned}
 H(\{r_i, p_i\}_{i=\overline{1,N}}) &= \sum_1^N \frac{p_i^2}{2m_i} + W_{AA}(\{r_i\}_{i=\overline{1,n}}) \\
 &\quad + W_{BB}(\{r_j\}_{j=\overline{n+1,N}}) + W_{AB}(\{r_i\}_{i=\overline{1,N}}) \\
 &\quad + \Phi_A(\{r_i\}_{i=\overline{1,n}}) + \Phi_B(\{r_i\}_{i=\overline{n+1,N}}) \quad (2.3)
 \end{aligned}$$

The equations of motion for the subset A are

$$m_i \ddot{r}_{i,\alpha} = - \frac{\partial}{\partial r_{i,\alpha}} (W_{AA} + \Phi_A) - \frac{\partial}{\partial r_{i,\alpha}} (W_{AB}), \quad i = \overline{1,n}, \alpha = \overline{1,3} \quad (2.4)$$

On the right-hand side of (2.4) the first term represents the mutual interactions of the A particles together with their coupling with the external field, while the last term gives their interactions with the solvent.

The essential simplification of the Langevin-type description of (2.4) consists in substituting the last term by a suitable stochastic description: this is precisely the spirit of Eq. (1.1).

The Mori technique can be applied choosing as the set of dynamical variables the column vector

$$\begin{aligned}
 (\underline{\mathbf{X}})_{i,\alpha} &= \left[\underline{\mathbf{p}} - \int_{-\infty}^t dt' \underline{\mathbf{F}}(t') \right]_{i,\alpha} \\
 &= p_{i,\alpha}(t) - \int_{-\infty}^t dt' F_{i,\alpha}(t'), \quad i = \overline{1,n}, \alpha = \overline{1,3} \quad (2.5)
 \end{aligned}$$

with

$$F_{i,\alpha} = - \frac{\partial}{\partial r_{i,\alpha}} (W_{AA} + \Phi_A) = \sum_{\substack{j \\ \neq i}} F_{\alpha}^{ij} (|r_j - r_i|) + F_{\alpha}^{\text{ext}}(\mathbf{r}_i)$$

(2.5) can also be written

$$\underline{\mathbf{X}}(t) = \underline{\mathbf{p}}(t) - (iL)^{-1} \underline{\mathbf{F}}(t) \quad (2.5a)$$

where $iL = \{H, \dots\}$ is the Liouville operator of the n particle system. The set of dynamical variables (2.5) satisfies the requirements (i) and (ii). Therefore, they satisfy Eq. (2.1), which can be written

$$\dot{\underline{\mathbf{p}}}(t) - \underline{\mathbf{F}}(t) = - \int_0^t dt' \underline{\mathbf{\Gamma}}(t-t') [\underline{\mathbf{p}}(+)(t') - (iL)^{-1} \underline{\mathbf{F}}(t')] + \underline{\mathbf{R}}(t) \quad (2.6)$$

where $\underline{\mathbf{R}}(t)$, the random force associated with the set (2.5), satisfies properties (2.2). Note that in (2.2c), the normalization matrix is not $\langle \underline{\mathbf{p}} \underline{\mathbf{p}}^T \rangle$ but $\langle [\underline{\mathbf{p}} - (iL)^{-1} \underline{\mathbf{F}}] [\underline{\mathbf{p}} - (iL)^{-1} \underline{\mathbf{F}}]^T \rangle$.

Defining a new random force $\underline{\mathbf{R}}'(t)$ as

$$\underline{\mathbf{R}}'(t) = \underline{\mathbf{R}}(t) + \int_0^t dt' \underline{\mathbf{\Gamma}}(t-t') \int_{-\infty}^{t'} dt'' \underline{\mathbf{F}}(t'') \quad (2.7)$$

Equation (2.6) becomes

$$\dot{\underline{\mathbf{p}}}(t) = - \int_0^t dt' \underline{\Gamma}(t-t') \underline{\mathbf{p}}(t') + \underline{\mathbf{R}}'(t) + \underline{\mathbf{F}}(t) \quad (2.8)$$

which looks formally identical to (1.1).

However, some of the most characteristic properties of a random force are lost; in particular, (2.2a) and (2.2b) are still valid, while (2.2c) and (2.2d) become, respectively,

$$\begin{aligned} \langle \underline{\mathbf{R}}'(t) \underline{\mathbf{R}}'^T(0) \rangle &= \underline{\Gamma}(t) \langle \underline{\mathbf{X}} \underline{\mathbf{X}}^T \rangle^{-1} \\ &+ \int_0^t dt' \underline{\Gamma}(t-t') \int_{-\infty}^{t'} dt'' \langle \underline{\mathbf{F}}(t'') \underline{\mathbf{F}}_{AB}^T(0) \rangle \end{aligned} \quad (2.9)$$

where

$$\underline{\mathbf{F}}_{AB} = - \frac{\partial}{\partial \underline{\mathbf{r}}} W_{AB}$$

and

$$\begin{aligned} \langle \underline{\mathbf{R}}'(t) \underline{\mathbf{p}}^T(0) \rangle &= \langle \dot{\underline{\mathbf{p}}}(t) \underline{\mathbf{p}}^T(0) \rangle - \langle \underline{\mathbf{F}}(t) \underline{\mathbf{p}}^T(0) \rangle \\ &+ \int_0^t dt' \underline{\Gamma}(t-t') \langle \underline{\mathbf{p}}(t') \underline{\mathbf{p}}^T(0) \rangle \end{aligned} \quad (2.10)$$

Equations (2.8) and (2.9) are the main results of this section. They show that while Eq. (1.1) can be obtained by an exact statistical mechanics derivation, the random force and the memory kernel so introduced do not satisfy the usual fluctuation-dissipation theorem but the more complicated relation (2.9). Moreover, the random force $\underline{\mathbf{R}}'(t)$ is not orthogonal to $\underline{\mathbf{p}}(0)$.

We now turn our attention to the physical exploitation of this GLE; we will see in the next sections that the form (2.6) of the GLE gives a much better starting point to the physical interpretation and to the GBD numerical implementation.

3. PHYSICAL INTERPRETATION

The time derivative of the chosen set of dynamical variables (2.5), $\dot{\underline{\mathbf{p}}}(t) - \underline{\mathbf{F}}(t)$, represents nothing else than the solute-solvent force $\underline{\mathbf{F}}_{AB}(t)$. This means that

$$\underline{\mathbf{X}}(t) = (iL)^{-1} \underline{\mathbf{F}}_{AB}(t) = \int_{-\infty}^t dt' \underline{\mathbf{F}}_{AB}(t') \quad (3.1)$$

Therefore,

$$\underline{\mathbf{C}}(t) \equiv \langle \underline{\mathbf{X}}(t) \underline{\mathbf{X}}^T(0) \rangle = - \int_t^\infty dt' \int_{t'}^\infty dt'' \langle \underline{\mathbf{F}}_{AB}(t'') \underline{\mathbf{F}}_{AB}^T(0) \rangle \quad (3.2)$$

By using the standard procedure of derivation of the first fluctuation-dissipation theorem,^(12a) we obtain

$$\underline{\tilde{C}}(z) = [z + \underline{\tilde{\Gamma}}(z)]^{-1} \underline{C}(0) \quad (3.3)$$

where $\underline{\tilde{C}}(z)$ and $\underline{\tilde{\Gamma}}(z)$ are the usual Laplace transforms of the $\underline{C}(t)$ and $\underline{\Gamma}(t)$ matrices.

Equations (3.2) and (3.3) taken together provide the natural link between the memory kernel $\underline{\Gamma}$ and the autocorrelation function of the solvent-solute force, which is a well-defined observable quantity. Therefore from the analysis of the hydrodynamical interactions for a given system (e.g., by molecular dynamics simulation) it is possible to arrive at a definite model for $\underline{\Gamma}$.

Until now by mutual interaction between Brownian particles we have always meant *bare* interaction. However, in some work^(1,4) of an applicative character the energy W_{AA} has been replaced by an *effective* interaction potential, usually obtained on a phenomenological basis.

The necessity of such a generalization has been quite clearly explained in a paper by Chandler and Pratt⁽¹⁶⁾ and recommended by Adelman.⁽⁹⁾ However, in Ref. 16 the aim was not to derive the corresponding GLE: some argument is given only for the choice of the effective potential. In the context of our derivation, given the W_{AA}^{eff} , it is quite easy to derive on a statistical mechanics basis the corresponding GLE. In fact, it is sufficient to choose as dynamical variable to be projected the new set of $\{\underline{X}^i\}$ given by

$$\underline{X}^i(t) = \underline{p}(t) - \int_{-\infty}^t dt' \underline{F}^{\text{eff}}(t') \quad (3.4)$$

where

$$\underline{F}^{\text{eff}} = - \frac{\partial}{\partial \underline{r}} W_{AA}^{\text{eff}}$$

Then the previous argument provides a GLE formally identical to (2.6) but with \underline{F} substituted by $\underline{F}^{\text{eff}}$. However, the physical interpretation of the kernel $\underline{\Gamma}$ corresponding to this new case is more obscure because it is tied to the autocorrelation function of $(\underline{\dot{p}} - \underline{F}^{\text{eff}})$ which, because of the phenomenological character of $\underline{F}^{\text{eff}}$, is a much less evident dynamical variable.

4. NUMERICAL IMPLEMENTATION

The next problem is to perform the GBD for the GLE (2.6). This consists in computing numerically the trajectory in the reduced phase space of the n Brownian particles according to the system

$$\begin{aligned} \underline{M}\dot{\underline{r}} &= \underline{p} & \text{with } M_{ij} &= m_i \delta_{ij} \\ \dot{\underline{p}} &= \underline{A}_1(t) + \underline{F}(\underline{r}) \end{aligned} \quad (4.1)$$

where $\underline{A}_1(t)$ defined by comparison with (2.6) is one of a set of (vectorial) auxiliary variables to be defined later. The stochastic character of (4.1) is given through $\underline{A}_1(t)$, which plays the role of a known time-dependent external force. Therefore the integration of (4.1) reduces to (i) the generation of $A_1(t)$ and (ii) the computation of $\underline{r}(t)$, $\underline{p}(t)$ by any suitable algorithm. As (ii) constitutes a standard matter, let us concentrate on (i).

To our knowledge^(9,10) the generation of $A_1(t)$ can be realized under two restrictive conditions: (i) The random force process is taken to be Gaussian, and (ii) the Mori continued fraction expansion^(12b) of $\underline{\Gamma}$ can be approximated in a satisfactory way by a truncated one. The technique is quite simple and has been described elsewhere for the scalar case.⁽¹⁰⁾ Here we present its extension to the general vectorial case. The essential steps go as follows.

It is well known^(12b) that the random force in (2.6) generates a family of random forces $\{\underline{R}_\lambda\}_{\lambda=\overline{1,\infty}}$ satisfying a usual GLE,

$$\dot{\underline{R}}_\lambda(t) = - \int_0^t dt' \underline{\Gamma}_{\lambda+1}(t-t') \underline{R}_\lambda(t') + \underline{R}_{\lambda+1}(t) \quad (4.2)$$

where

$$\underline{R}_1(t) \equiv \underline{R}(t) \quad \text{and} \quad \underline{\Gamma}_1(t) = \underline{\Gamma}(t).$$

The family of kernels $\underline{\Gamma}_\lambda(t)$ satisfies the set of equations

$$\dot{\underline{\Gamma}}_\lambda(t) = - \int_0^t dt' \underline{\Gamma}_{\lambda+1}(t-t') \underline{\Gamma}_\lambda(t') \quad (4.3)$$

Let us now introduce⁽¹⁰⁾ the set of auxiliary variables $\{\underline{A}_\lambda\}_{\lambda=\overline{0,\infty}}$

$$\dot{\underline{A}}_\lambda(t) = - \int_0^t dt' \underline{\Gamma}_\lambda(t-t') \underline{A}_{\lambda-1}(t') + \underline{R}_\lambda(t) \quad (4.4)$$

with $\underline{A}_0(t) \equiv \underline{X}(t)$. Note that $\underline{A}_1(t)$ has been defined in (4.1) according (4.4). Combining (4.2), (4.3), and (4.4) it is easy to show that the $\{\underline{A}_\lambda\}$ satisfies the following evolution equations:

$$\dot{\underline{A}}_\lambda = - \underline{\Gamma}_\lambda(0) \underline{A}_{\lambda-1}(t) + \underline{A}_{\lambda+1}(t) \quad (4.5)$$

Then, in principle, $\underline{A}_1(t)$ can be generated by solving the infinite set

$$\begin{aligned} \dot{\underline{A}}_0(t) &= \underline{A}_1(t) \\ \dot{\underline{A}}_\lambda(t) &= - \underline{\Gamma}_\lambda(0) \underline{A}_{\lambda-1}(t) + \underline{A}_{\lambda+1}(t), \quad \lambda = \overline{1,\infty} \end{aligned} \quad (4.6)$$

In fact this is all but an easy job. However, if the random force of order ν can be approximated by a Gaussian white noise $\underline{\xi}(t)$ such that $\underline{\Gamma}_\nu(t) = 2 \underline{\beta} \delta(t)$, then the infinite set (4.6) is truncated at the order $\nu - 1$ by

$$\dot{\underline{A}}_{\nu-1}(t) = - \underline{\Gamma}_{\nu-1}(0) \underline{A}_{\nu-2}(t) - \underline{\beta} \underline{A}_{\nu-1}(t) + \underline{\xi}(t) \quad (4.7)$$

The resulting finite system can be seen as a vectorial strict Langevin

equation replacing (2.6) and can be easily implemented on a computer to generate $\underline{A}_1(t)$.

Coming back to (4.1) it is possible now to integrate them explicitly to get realizations of the stationary process $\{r_{i,\alpha}, p_{i,\alpha}\}$, $i = \overline{1, n}$, $\alpha = \overline{1, 3}$, generating the phase space trajectory in the subspace of the n Brownian particles. This permits the evaluation of equilibrium or dynamical properties of these n particles in a bath.

5. CONCLUSIONS

Formulas (2.6), (3.2), and (3.3) constitute the main results of this paper. They give a derivation à la Mori and a physical interpretation of a nonlinear GLE for interacting particles in a bath. Equation (2.6), which is basic to all BD and GBD simulations, provides a quite natural separation of the mutual interactions of the Brownian particles from the heat bath solvent interactions which are treated stochastically. The second fluctuation-dissipation theorem relates the kernel of the convolution term in (2.6) to the solvent-solute force autocorrelation function [Eqs. (3.2) and (3.3)]. It gives in a clearcut way the physical meaning of the random force. For GBD purposes we have sketched in Section 4 a suitable procedure. The validity of it rests on two main approximations: (i) the random force is modeled by a stationary Gaussian process, and (ii) the continued fraction representation of the memory kernel $\underline{\Gamma}$ can be truncated at some finite order. In general the kernel $\underline{\Gamma}$ is a matrix; if it is diagonal the stochastic part of the problem reduces to the scalar case, which has been described extensively elsewhere.⁽¹⁰⁾ In the general case Section 4 shows how to adapt the technique.

The definition (2.5) of the dynamical variable that we have chosen to apply the Mori projection technique is such that the presence of an external stationary field is in the scope of our derivation. Therefore the same kind of arguments we have presented before apply to the case of a single particle subjected to a stationary external field, say, for example, an ion in a fluid in presence of an electrical and magnetic field. However, our argument fails if the external field is explicitly time dependent. In this case, the system is not in equilibrium and the Mori projection technique does not apply. Moreover there is in general no clear way to extend Mori's ideas: this is only possible in the very special case where the external force is an impulsive one, that is, where the time dependence is given through a δ function type of behavior, $\Phi(t) \sim \delta(t)$. Here the physical meaning of the force is simply a suitable choice of the initial conditions and the GLE gives the relaxation of the variable $X(t)$ toward equilibrium. Often⁽¹⁷⁾ a GLE has been written on intuitive grounds for general time-dependent forces in the validity region of

linear response theory (LRT). In this case the GLE gives simply a rephrasing of LRT and no special meaning has to be attached to the corresponding GLE. From the formal point of view there is not much more to be added. However, from the physical point of view some comments are in order.

In the framework of Mori the time evolution of the random force is far from simple. Indeed it contains all but the systematic force, i.e., the convolution term of the GLE, and it is quite improbable that $R(t)$ can be reduced to a Gaussian process. On the other hand the aim of GBD both for technical and physical reasons consists just in the reduction of the random force to some kind of simple stochastic process, after extraction of all the relevant properties of the degrees of freedom to be disregarded (the thermal bath of above). Therefore some bridge has to be built to fill this gap. We believe that a solution to this problem could come from two main sources. The first one consists in replacing the bare forces of Eq. (2.6) with some "renormalized" ones representing an effective interaction and/or external field. The systematic derivation of such an effective potential is, to our knowledge, still missing. Moreover, as has been discussed at the end of Section 3, the physical meaning of the random force autocorrelation function is in this case far from clear. A proper derivation of the effective potential could be of great help in clarifying this last point.

The second possibility to be considered consists in changing the projection technique so as to include in the systematic force all the properties of the bath relevant for the evolution of the Brownian subsystem under study. This could be obtained by applying the Deutch and Oppenheim⁽¹³⁾ technique of hydrodynamic interactions. The main problem here is the introduction of memory effects in the corresponding strict Langevin equation. This generalization is still lacking.

ACKNOWLEDGMENTS

It is a pleasure to thank M. De Leener and B. Quentrec for useful discussions. We wish to thank also A. Bellemans for a critical reading of the manuscript. This work has been partially supported by a NATO Research Grant No. 1865.

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