Journal of Statistical Physics, Vol. 38, Nos. 3/4, 1985

Augmented Langevin Approach to Fluctuations in Nonlinear Irreversible Processes

John D. Ramshaw[1]

Received June 27, 1984

A Fokker–Planck equation derived from statistical mechanics by M. S. Green [*J. Chem. Phys.* **20**:1281 (1952)] has been used by Grabert *et al.* [*Phys. Rev. A* **21**:2136 (1980)] to study fluctuations in nonlinear irreversible processes. These authors remarked that a phenomenological Langevin approach would not have given the correct reversible part of the Fokker–Planck drift flux, from which they concluded that the Langevin approach is untrustworthy for systems with partly reversible fluxes. Here it is shown that a simple modification of the Langevin approach leads to precisely the same covariant Fokker–Planck equation as that of Grabert *et al.*, including the reversible drift terms. The modification consists of augmenting the usual nonlinear Langevin equation by adding to the deterministic flow a correction term which vanishes in the limit of zero fluctuations, and which is self-consistently determined from the assumed form of the equilibrium distribution by imposing the usual potential conditions. This development provides a simple phenomenological route to the Fokker–Planck equation of Green, which has previously appeared to require a more microscopic treatment. It also extends the applicability of the Langevin approach to fluctuations in a wider class of nonlinear systems.

KEY WORDS: Langevin equation; Fokker–Planck equation; fluctuation–dissipation theorem; fluctuations; noise; irreversible processes; nonlinear dynamics.

1. INTRODUCTION

In contrast to linear irreversible thermodynamics,[1,2] whose proper formulation is well established and generally accepted, the theory of nonlinear irreversible processes is still in a state of flux. Nevertheless, the *deterministic* nonlinear theory has acquired a rather conventional

[1] Theoretical Division, University of California, Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

0022-4715/85/0200-0669$04.50/0

formulation in which the equations of motion for the relevant macroscopic variables $\mathbf{x} = (x_1, x_2, ..., x_n)$ are written in the generalized Onsager form[3,4]

$$\dot{\mathbf{x}} = \mathsf{L}(\mathbf{x}) \cdot \nabla S(\mathbf{x}) \tag{1}$$

where $S(\mathbf{x})$ is the entropy of the macrostate $\mathbf{x}$, and $\nabla = \partial/\partial\mathbf{x}$. The transport matrix $\mathsf{L}(\mathbf{x})$ may be resolved into symmetric and antisymmetric parts,

$$\mathsf{L}(\mathbf{x}) = \mathsf{D}(\mathbf{x}) + \mathsf{A}(\mathbf{x}) \tag{2}$$

$$\mathsf{D}(\mathbf{x}) = \tfrac{1}{2}[\mathsf{L}(\mathbf{x}) + \mathsf{L}^T(\mathbf{x})] \tag{3}$$

$$\mathsf{A}(\mathbf{x}) = \tfrac{1}{2}[\mathsf{L}(\mathbf{x}) - \mathsf{L}^T(\mathbf{x})] \tag{4}$$

where superscript T denotes the transpose. The antisymmetric matrix $\mathsf{A}(\mathbf{x})$ generates the ideal or reversible part of the dynamics (e.g., convection terms and pressure forces), while the symmetric matrix $\mathsf{D}(\mathbf{x})$ generates the dissipative part (e.g., viscous and friction terms). These interpretations follow from the fact that the time rate of change of the entropy is

$$\dot{S} = \nabla S \cdot \mathsf{D} \cdot \nabla S \tag{5}$$

to which A does not contribute and which vanishes if $\mathsf{D} = 0$. The second law of thermodynamics requires that D be positive definite.

The above deterministic description does not allow for fluctuations in the variables $\mathbf{x}$ that arise from couplings to the microscopic degrees of freedom not included in the macrostate. The introduction of fluctuations makes $\mathbf{x}(t)$ a random process. Under the assumption that this process is Markovian, M. S. Green[5] derived from statistical mechanics a Fokker–Planck equation for $\rho(\mathbf{x}, t)$, the probability distribution of the variables $\mathbf{x}$ at time t. A more systematic statistical-mechanical derivation was subsequently given by Zwanzig[6,7] using projection-operator techniques. In the covariant formulation of Grabert, Graham, and Green[3] (GGG), this Fokker–Planck equation takes the form

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathsf{L} \cdot \nabla S) = k_B \nabla \cdot [\nabla \cdot (\rho \mathsf{D}) - \rho g^{1/2} \nabla \cdot (g^{-1/2} \mathsf{L}^T)] \tag{6}$$

where k_B is Boltzmann's constant and $g(\mathbf{x})$ is the determinant of a metric tensor in state space. This equation admits the stationary solution

$$w(\mathbf{x}) = w_0 \, g^{-1/2}(\mathbf{x}) \exp\left[S(\mathbf{x})/k_B - \sum_i \beta_i B_i(\mathbf{x}) \right] \tag{7}$$

where the $B_i(\mathbf{x})$ are constants of the motion that are separately conserved by both the ideal and dissipative parts of the dynamics, so that

$$\mathsf{A} \cdot \nabla B_i = \mathsf{D} \cdot \nabla B_i = 0 \tag{8}$$

and the β_i are arbitrary constants. The normalization constant w_0 is to be chosen so that $\int d\mathbf{x}\, w(\mathbf{x}) = 1$.

The derivations of Green and Zwanzig were based on statistical mechanics. A more common way of obtaining Fokker–Planck equations is the phenomenological approach of postulating an appropriate Langevin equation (usually by adding a white noise term to the deterministic dynamics) and converting it to the equivalent Fokker–Planck equation.[8,9] It is natural to inquire whether Eq. (6) can be obtained in this way, thereby circumventing the need for a fully microscopic derivation. This question was briefly considered by GGG, who thought that the answer must in general be negative. The reason given was that the term $\rho g^{1/2} \nabla \cdot (g^{-1/2}\mathsf{A})$ appearing in Eq. (6) would not properly arise in the Langevin treatment, and GGG concluded on this basis that the phenomenological Langevin approach is untrustworthy for systems with partly reversible fluxes (i.e., nonzero A).

Our purpose here is to present a simple and natural modification of the Langevin approach which, when applied to the dynamical system of Eq. (1), leads precisely to Eq. (6). The appropriate modification is suggested by van Kampen's observation[10] that in a nonlinear Langevin equation of the form $\dot{\mathbf{x}} = \mathbf{A}(\mathbf{x}) + \mathsf{G}(\mathbf{x}) \cdot \boldsymbol{\xi}(t)$ (where $\boldsymbol{\xi}(t)$ is white noise), the function $\mathbf{A}(\mathbf{x})$ is phenomenologically uncertain to within terms of the order of the fluctuations. Thus, instead of identifying $\mathbf{A}(\mathbf{x})$ with the function $\mathbf{U}(\mathbf{x})$ appearing in the deterministic dynamics $\dot{\mathbf{x}} = \mathbf{U}(\mathbf{x})$, one is free to set $\mathbf{A}(\mathbf{x}) = \mathbf{U}(\mathbf{x}) + \mathbf{F}(\mathbf{x})$, where $\mathbf{F}(\mathbf{x})$ is some function which vanishes in the limit of zero fluctuations. The function $\mathbf{F}(\mathbf{x})$ may then be determined from the assumed form of the equilibrium distribution by imposing the usual potential conditions.[3,9,11] In the present context, it will be seen that this procedure leads directly to Eq. (6) in a remarkably straightforward way.

The present development thereby provides a simple phenomenological route to the Fokker–Planck equation of M. S. Green, which has previously appeared to require a more microscopic derivation. It also extends the applicability of the Langevin approach to a wider class of fluctuating nonlinear systems. This lends increased confidence in the prospects for correct Langevin treatments of fluctuations in other nonlinear dissipative systems. Of course, we do not mean to minimize the notorious hazards of nonlinear Langevin equations, which have been quite properly emphasized by van Kampen.[10] It remains generally true that nonlinear Langevin equations must be used with extreme caution. But neither should one

minimize the fact that when used with care and some awareness of the pitfalls, such equations can lead to correct results in a very simple manner, as the present development illustrates. It now appears, in retrospect, that many of the earlier difficulties, which at first appeared to reflect fundamental shortcomings in the Langevin approach, were simply due to an insufficiently complete allowance for the phenomenological uncertainty in the Langevin function $\mathbf{A}(\mathbf{x})$.

2. CONVENTIONAL AND AUGMENTED NONLINEAR LANGEVIN EQUATIONS

We begin with a brief recapitulation of the conventional Langevin procedure for introducing fluctuations into a deterministic nonlinear dynamical system of the form

$$\dot{\mathbf{x}} = \mathbf{U}(\mathbf{x}) \tag{9}$$

In this procedure, one adds a white noise term to the deterministic dynamics to obtain

$$\dot{\mathbf{x}} = \mathbf{U}(\mathbf{x}) + \mathsf{G}(\mathbf{x}) \cdot \boldsymbol{\xi}(t) \tag{10}$$

where $\boldsymbol{\xi}(t)$ is an n-dimensional vector whose components are independent zero-mean normalized Gaussian white noises. Thus $\langle \boldsymbol{\xi}(t) \rangle = 0$ and $\langle \boldsymbol{\xi}(t)\, \boldsymbol{\xi}(t+\tau) \rangle = \mathsf{I}\delta(\tau)$, where I is the unit matrix and the angular brackets $\langle \cdots \rangle$ denote an appropriately weighted ensemble average over all possible realizations of $\boldsymbol{\xi}(t)$.

Since the coefficient of $\boldsymbol{\xi}(t)$ in Eq. (10) depends on $\mathbf{x}$, an interpretation rule is needed[10] which we take to be that of Stratonovich. The Stratonovich rule is appropriate if we regard the white noise as the limit of colored noise for vanishing autocorrelation time, and it has the desirable feature that nonlinear transformations of the stochastic variables may be performed by the ordinary rules of calculus.[10] With this interpretation, the Fokker–Planck equation equivalent to Eq. (10) is[8,9]

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \mathbf{U}) = \tfrac{1}{2} \boldsymbol{\nabla} \cdot \{ \mathsf{G} \cdot [\boldsymbol{\nabla} \cdot (\rho \mathsf{G})] \} \tag{11}$$

The crux of this approach is clearly the proper identification of $\mathbf{U}$ and G. Evidently $\mathbf{U}$ governs the dynamics in the absence of fluctuations, but frequently the fluctuations are intrinsic ("internal noise") and $\mathbf{U}$ is not directly accessible. In such cases, all that is known is the dynamics with fluctuations present, expressed in the form of phenomenological equations of

motion $\langle \dot{\mathbf{x}} \rangle = \mathbf{U}^*(\langle \mathbf{x} \rangle)$ for the mean values. Because of the nonlinearity, the identification of $\mathbf{U}$ with $\mathbf{U}^*$ is not permissible[10]; the difference may be regarded as a fluctuation renormalization effect.[7,12–16] In this situation, the usual phenomenological practice has been to assume that $\mathbf{U}$ and $\mathbf{U}^*$ have essentially the same mathematical *form* but differ in the values of the various parameters (e.g., viscosities, friction coefficients, etc.) appearing therein. (The function $\mathbf{U}$ contains "bare" parameters λ_i, while $\mathbf{U}^*$ contains corresponding "renormalized" parameters λ_i^*. It is the λ_i^* that are measured in ordinary experiments governed by the mean equations of motion.) This assumption determines the form of $\mathbf{U}$ but not the bare parameters λ_i, which remain phenomenologically undetermined and are therefore to be regarded as adjustable parameters in the theory. For given values of the λ_i, one then attempts to choose G in such a way that Eq. (11) admits the known equilibrium distribution as a stationary solution. If desired, one can go on to derive approximate closed equations for $\langle \mathbf{x} \rangle$ from Eq. (11) by fluctuation renormalization techniques.[7,12–16] This then establishes the connection between the λ_i and λ_i^*, and if the latter are known from experimental measurements one can hope to infer the corresponding values of the former.

The problem with the conventional approach just outlined is that one has no real basis for assuming that the Langevin equation should contain a function of even the same *form* as $\mathbf{U}^*$. As emphasized by van Kampen,[10] all that can safely be said is that the function appearing in the Langevin equation is inherently uncertain, from a phenomenological point of view, to within terms of the order of the fluctuations. In general, there is no reason to suppose that this uncertainty does not involve differences in functional form as well as a renormalization of parameters.

Up until now, this uncertainty has apparently been regarded simply as a basic flaw in the Langevin approach to nonlinear problems. We propose instead to make it the basis of an augmented Langevin approach in which the phenomenological uncertainty is explicitly recognized from the outset and used to advantage. In this approach, Eq. (10) is replaced by

$$\dot{\mathbf{x}} = \mathbf{U}(\mathbf{x}) + \mathbf{F}(\mathbf{x}) + \mathsf{G}(\mathbf{x}) \cdot \boldsymbol{\xi}(t) \tag{12}$$

where $\mathbf{U}(\mathbf{x})$ is identified just as in the conventional Langevin approach, and $\mathbf{F}(\mathbf{x})$ is an as yet undetermined correction term which is required to vanish in the limit of zero fluctuations (i.e., as $\mathsf{G} \to 0$). The inherent phenomenological uncertainty in the Langevin equation is now explicitly recognized by the presence of $\mathbf{F}(\mathbf{x})$, which by definition is a term of the order of the fluctuations. The Fokker–Planck equation equivalent to Eq. (12) is

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \mathbf{U}) + \boldsymbol{\nabla} \cdot (\rho \mathbf{F}) = \tfrac{1}{2} \boldsymbol{\nabla} \cdot \{\mathsf{G} \cdot [\boldsymbol{\nabla} \cdot (\rho \mathsf{G})]\} \tag{13}$$

For given values of the λ_i, one now attempts to choose *both* F and G in such a way that Eq. (13) admits the known equilibrium distribution as a stationary solution. The manner in which this is done will become clear in the next section.

Equation (13) may be rewritten as

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{U}) + \nabla \cdot (\rho \mathbf{V}) = \tfrac{1}{2} \nabla \cdot (\Gamma \cdot \nabla \rho) \tag{14}$$

where $\Gamma(\mathbf{x}) = \mathsf{G}(\mathbf{x}) \cdot \mathsf{G}^T(\mathbf{x})$ and

$$\mathbf{V}(\mathbf{x}) = \mathbf{F}(\mathbf{x}) - \tfrac{1}{2} \mathsf{G}(\mathbf{x}) \cdot [\nabla \cdot \mathsf{G}(\mathbf{x})] \tag{15}$$

Since **F** is required to vanish as $\mathsf{G} \to 0$ the same is true of **V**, and we can henceforth regard **V** rather than **F** as the auxiliary vector to be determined. Once **V** supersedes **F**, G enters into Eq. (14) only through the symmetric positive definite matrix Γ, and there is no loss of generality in supposing G to be symmetric and positive definite as well. Then G is just the positive square root of Γ, and knowledge of Γ is equivalent to knowledge of G. Now, instead of focusing directly on **F** and G, one determines **V** and Γ in such a way that the known equilibrium distribution is a steady solution of Eq. (14). The positive square root of Γ is then identified with G, and G together with **V** determines **F** via Eq. (15). All quantities in the augmented Langevin equation (12) are then known, and the physical situation of interest can be studied by means of either Eq. (12) or Eq. (14), whichever is more convenient.

Although we have adopted the Stratonovich interpretation of stochastic equations such as Eq. (12), the augmented Langevin approach yields equivalent results when the Itô interpretation[10] is used. This is a consequence of the presence of **F** in the formulation, and is not true for the conventional Langevin approach. The reason for the equivalence is that if Eq. (12) were interpreted in the Itô sense, Eq. (14) would still obtain but with $\mathsf{G} \cdot (\nabla \cdot \mathsf{G})$ replaced by $\nabla \cdot \Gamma$ in Eq. (15). However, this different relation between **F** and **V** does not affect the determination of **V** and Γ, which quantities will therefore have the same values as before so that the same Fokker–Planck equation results. The change in Eq. (15) *does* affect the value of **F**, but that is because Eq. (12) has become an Itô equation; the change in **F** simply effects the conversion from a given Stratonovich equation to an equivalent Itô equation. Our somewhat arbitrary adoption of the Stratonovich interpretation therefore does not give rise to any corresponding arbitrariness in the final results. The augmented Langevin approach consequently has the desirable and advantageous feature that the choice of stochastic interpretation rule is devoid of physical consequences, in contrast to the conventional Langevin approach.[10]

3. AUGMENTED LANGEVIN DERIVATION OF GREEN'S FOKKER–PLANCK EQUATION

We now proceed to apply the augmented Langevin approach to the generalized Onsager dynamics of Eq. (1). We first set $\mathbf{U} = \mathsf{L} \cdot \nabla S$, whereupon Eq. (14) becomes

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathsf{L} \cdot \nabla S) + \nabla \cdot (\rho \mathbf{V}) = \tfrac{1}{2} \nabla \cdot (\Gamma \cdot \nabla \rho) \tag{16}$$

Next we require that the equilibrium distribution $w(\mathbf{x})$ of Eq. (7) be a stationary solution of Eq. (16). This requirement will be met by imposing the potential conditions[3,9,11]

$$\nabla \cdot [w(\mathsf{A} \cdot \nabla S + \mathbf{V}_R)] = 0 \tag{17}$$

$$w(\mathsf{D} \cdot \nabla S + \mathbf{V}_I) = \tfrac{1}{2} \Gamma \cdot \nabla w \tag{18}$$

where $\mathbf{V}_R + \mathbf{V}_I = \mathbf{V}$. These conditions are sufficient but not necessary for w to be stationary. Their physical justification lies in their equivalence to the property of detailed balance.[9,11] Detailed balance is not a universal property of stationary distributions,[9,10,17] but it is a general feature of true thermodynamic equilibrium[1,9,10] and this suffices for its applicability in the present context. Detailed balance is also quite common in nonequilibrium steady states as a consequence of symmetry constraints on transition rates.[9]

The first potential condition, Eq. (17), states that the stationary distribution would remain stationary even in the absence of irreversibility. The second potential condition, Eq. (18), states that the irreversible part of the probability flux (and not merely its divergence) vanishes in steady state. Since there is no apparent reason to suppose that the vector $\mathbf{V}$ is purely reversible or irreversible in nature, it has been resolved into a reversible part $\mathbf{V}_R$ and an irreversible part $\mathbf{V}_I$, which will need to be determined separately. Their sum then gives the vector $\mathbf{V}$ to be used in Eq. (16).

Equation (18) can be explicitly solved for $\mathbf{V}_I$, with the result

$$\mathbf{V}_I = \left(\frac{1}{2k_B} \Gamma - \mathsf{D} \right) \cdot \nabla S + \tfrac{1}{2} \Gamma \cdot \left(g^{1/2} \nabla g^{-1/2} - \sum_i \beta_i \nabla B_i \right) \tag{19}$$

Now $\mathbf{V}_R$ and $\mathbf{V}_I$ are independent, so they must separately vanish in the limit of zero fluctuations. But Eq. (19) for $\mathbf{V}_I$ contains a term $-\mathsf{D} \cdot \nabla S$ which involves only deterministic quantities that are independent of the size of the fluctuations. To prevent this term from contributing to $\mathbf{V}_I$, we impose the nonlinear fluctuation–dissipation relation

$$\Gamma(\mathbf{x}) = 2k_B \mathsf{D}(\mathbf{x}) \tag{20}$$

Since Γ also vanishes in the limit of zero fluctuations, Eq. (20) shows that a self-consistent passage to this limit requires $k_B \to 0$ as well.[3,4] Once this connection is established, letting $k_B \to 0$ is in fact the most convenient way to take the limit. It then follows from Eq. (20) that Γ vanishes like k_B (and hence G vanishes like $k_B^{1/2}$) as $k_B \to 0$. By virtue of Eqs. (20) and (8), Eq. (19) now reduces to

$$\mathbf{V}_I = k_B\, g^{1/2} \mathsf{D} \cdot \nabla g^{-1/2} \tag{21}$$

The determination of $\mathbf{V}_R$ proceeds in a similar manner. Combining Eqs. (7) and (17) and making use of Eq. (8), we obtain

$$\nabla \cdot (g^{-1/2}\mathbf{V}_R) = g^{-1/2}\mathbf{V}_R \cdot \sum_i \beta_i \nabla B_i - \left[\nabla \cdot (g^{-1/2}\mathsf{A}) + \frac{1}{k_B}\, g^{-1/2}\mathbf{V}_R\right] \cdot \nabla S \tag{22}$$

But Eq. (22) contains a source term $[\nabla \cdot (g^{-1/2}\mathsf{A})] \cdot \nabla S$ which involves only deterministic quantities that are independent of the size of the fluctuations. To prevent this term from making a contribution to $\mathbf{V}_R$ which does not properly vanish as $k_B \to 0$, we impose the condition

$$\nabla \cdot (g^{-1/2}\mathsf{A}) + \frac{1}{k_B}\, g^{-1/2}\mathbf{V}_R = 0 \tag{23}$$

which is evidently a reversible analog of the fluctuation–dissipation relation (20). However, Eq. (20) did not directly involve $\mathbf{V}_I$, whereas the condition (23) already implies that $\mathbf{V}_R$ must be given by

$$\mathbf{V}_R = -k_B\, g^{1/2} \nabla \cdot (g^{-1/2}\mathsf{A}) \tag{24}$$

and it is necessary to verify that this $\mathbf{V}_R$ is actually a solution of the full Eq. (22). One readily verifies that Eq. (24) does in fact satisfy Eq. (22), because

$$\nabla \cdot (g^{-1/2}\mathbf{V}_R) = -k_B \nabla\nabla : (g^{-1/2}\mathsf{A}) = 0 \tag{25}$$

and

$$g^{-1/2}\mathbf{V}_R \cdot \nabla B_i = -k_B [\nabla \cdot (g^{-1/2}\mathsf{A})] \cdot \nabla B_i = 0 \tag{26}$$

where use has been made of Eq. (8) and the antisymmetry of A.

Combining $\mathbf{V}_R$ and $\mathbf{V}_I$, we obtain

$$\mathbf{V} = \mathbf{V}_R + \mathbf{V}_I = k_B\, g^{1/2} [\mathsf{D} \cdot \nabla g^{-1/2} - \nabla \cdot (g^{-1/2}\mathsf{A})] \tag{27}$$

The final Fokker–Planck equation is obtained by combining Eqs. (20) and (27) with Eq. (16). When this is done we obtain, after a little algebra,

precisely the Fokker–Planck equation of M. S. Green, Eq. (6). The corresponding Langevin equation is Eq. (12), in which G is the positive square root of Γ, and $\mathbf{F}$ is obtained from $\mathbf{V}$ by Eq. (15).

4. CONCLUDING REMARKS

We have described an augmented Langevin approach to fluctuations in nonlinear irreversible systems, which is a simple and natural extension of the conventional Langevin approach. Application of the augmented Langevin approach to the generalized Onsager formulation of nonlinear irreversible thermodynamics has been shown to lead directly to the Fokker–Planck equation of M. S. Green, which has previously appeared to require a more elaborate microscopic derivation. This lends support to the hope and expectation that the same approach will provide correct Langevin treatments of fluctuations in a broader class of nonlinear dissipative systems. The advantage of the augmented Langevin approach is that it is simple, straightforward, and physically transparent. Its disadvantage is that, like the conventional Langevin approach, it is purely phenomenological in nature, and the limits of its validity are therefore not at present known. (In particular, its applicability to systems without detailed balance is unclear.) Nevertheless, the augmented Langevin approach appears to be significantly broader in scope than the conventional Langevin approach, and further insight into its domain of validity may be expected to emerge as further applications and comparisons with microscopic theory are made.

Finally, it may be noted that even without the introduction of $\mathbf{F}(\mathbf{x})$ there is somewhat more freedom in the Langevin approach than is sometimes recognized. We refer to the freedom associated with the choice of the noise coefficient matrix $\mathrm{G}(\mathbf{x})$, which is customarily taken to be symmetric but need not be.[9] In fact, by imposing certain subsidiary conditions on $\mathrm{G}(\mathbf{x})$ it is possible to give a more conventional Langevin derivation of Eq. (6) without introducing $\mathbf{F}(\mathbf{x})$ at all, provided that $n \geqslant 3$. (The suggestion to the contrary by GGG appears to have been implicitly based on the simple subsidiary condition $\nabla \cdot (g^{-1/2}\mathrm{G}) = 0$, which is inappropriate here unless $\nabla \cdot (g^{-1/2}\mathrm{A}) = 0$ as well.) This approach is briefly summarized in an Appendix. It may at first seem preferable to the approach taken in the main development, as it appears to avoid the introduction and determination of the new quantity $\mathbf{F}(\mathbf{x})$. However, its appeal is specious. The fact that this approach breaks down for $n = 1$ and 2 is an indication that it is not really fundamental, and even for $n \geqslant 3$ the required subsidiary conditions on G are differential equations whose self-consistency and solvability are by no means obvious. The development using $\mathbf{F}(\mathbf{x})$ is actually simpler, as it eliminates the complicated subsidiary conditions on G. This enables the symmetry of G to

be preserved, and the determination of G is then simply an algebraic problem rather than a differential one. But more important than considerations of simplicity is the fact that the introduction of $\mathbf{F}(\mathbf{x})$ is in closer accord with the physics of the situation, as it directly reflects and exploits the inherent phenomenological uncertainty in the Langevin function $\mathbf{A}(\mathbf{x})$. Because of this uncertainty, it is inappropriate to force an identification of the Langevin $\mathbf{A}(\mathbf{x})$ with the deterministic $\mathbf{U}(\mathbf{x})$. The complicated subsidiary conditions on G given in the Appendix are artifacts of this forced identification and are devoid of physical significance; this awkwardness is completely eliminated by introducing $\mathbf{F}(\mathbf{x})$.

ACKNOWLEDGMENTS

I am grateful to Katja Lindenberg for thoughtful comments on the manuscript. This work was performed under the auspices of the U.S. Department of Energy.

APPENDIX

Here we wish to explore the consequences of introducing fluctuations into Eq. (1) by the conventional Langevin approach, in which $\mathbf{F} = 0$. We shall see that one can partially compensate for the absence of $\mathbf{F}$ by making maximum use of the available freedom in the choice of the noise coefficient matrix G.[9] Thus G will not here be taken to be symmetric and positive definite as it was in the main text. However, we shall also find that this compensation is ultimately unsatisfactory and the augmented Langevin approach is to be preferred.

The simplest way to proceed is to follow through the development of Section 3 with the understanding that now $\mathbf{F} = 0$ and G is asymmetric. This means that Eq. (15), which previously determined $\mathbf{F}$ in terms of $\mathbf{V}$ and G, must now be regarded as a set of subsidiary conditions on G in terms of $\mathbf{V}$. Combining Eqs. (15) and (27) and setting $\mathbf{F} = 0$, we obtain

$$\mathsf{G} \cdot (\boldsymbol{\nabla} \cdot \mathsf{G}) = -2k_B g^{1/2}[\mathsf{D} \cdot \boldsymbol{\nabla} g^{-1/2} - \boldsymbol{\nabla} \cdot (g^{-1/2}\mathsf{A})] \tag{A1}$$

Equation (20) still applies, with $\Gamma = \mathsf{G} \cdot \mathsf{G}^T$, so that Eq. (A1) may be rewritten in the equivalent form

$$\mathsf{G} \cdot [\boldsymbol{\nabla} \cdot (g^{-1/2}\mathsf{G})] = 2k_B \boldsymbol{\nabla} \cdot (g^{-1/2}\mathsf{A}) \tag{A2}$$

Since Γ and D are symmetric, Eq. (20) represents $\frac{1}{2}n(n+1)$ conditions on the n^2 elements of G. Equation (A2) constitutes a set of n additional subsidiary conditions on the elements of G. Barring accidental degeneracies, therefore,

the simultaneous satisfaction of all these conditions will be possible only when $n^2 \geqslant \frac{1}{2}n(n+1)+n$, i.e., $n \geqslant 3$. Thus for systems of three or more dependent variables, it is potentially possible to choose G in such a way that both Eqs. (20) and (27) continue to hold even with $\mathbf{F}=0$, so that Green's Fokker–Planck equation (6) continues to obtain. Of course, the actual solution for G is an unappealing prospect, since the subsidiary conditions of Eq. (A2) are a system of partial differential equations for the elements of G. Indeed, it is not even clear that these conditions are self-consistent, or if so that a solution can be found.

It is interesting to note that when $\nabla \cdot (g^{-1/2}\mathrm{A})=0$, Eq. (A2) reduces to the much simpler condition

$$\nabla \cdot (g^{-1/2}\mathrm{G})=0 \tag{A3}$$

which is the covariant analog of the condition $\nabla \cdot \mathrm{G}=0$ mentioned by Graham.[9] If one were to impose Eq. (A3) in general, Eq. (A2) would no longer be satisfied and hence Eq. (6) would no longer result. This appears to have been the basis for the statement by GGG that the Langevin approach may not be correct for nonlinear systems with partly reversible fluxes. The problem, however, lies not in the Langevin approach but in the use of an inappropriate subsidiary condition, Eq. (A3), instead of the proper one, Eq. (A2). Nevertheless, this conventional Langevin approach is still unsatisfactory, both because of the curious restriction to $n \geqslant 3$ and because of the complexity and inconvenience of the subsidiary conditions of Eq. (A2).

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