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A Comment on Chemical Langevin Equations

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It is noted that the diffusion Langevin stochastic sources in chemical reaction-diffusion theories should really arise from a stochastic source term added to the deterministic form of Fick's law. This gives rise to results for correlation functions which agree with those from stochastic master equations provided parameters are appropriately chosen.

KEY WORDS: Stochastic equations; Langevin equations; chemical reactions; diffusion theory; master equations; fluctuations.

Recently, chemical fluctuations have been studied from various points of view. It has been usual to write chemical Langevin equations for concentrations in the form

$$\frac{\partial\psi_i}{\partial t} = \mathbf{D}_i\nabla^2\psi_i + \left.\frac{\partial\psi_i}{\partial t}\right|_{\text{chem}} + g_i(\mathbf{x}, t) \tag{1}$$

where $g_i(\mathbf{x}, t)$ is a stochastic source[2] and $(\partial\psi_i/\partial t)|_{\text{chem}}$ is a certain function of the chemical concentrations, which describes the chemical process under consideration.

The statistics of the stochastic source term must be specified by fixing the correlation functions of the stochastic sources. These are often fixed in a rather arbitrary manner. For example, Nitzan *et al.*[(1)] use

$$\langle g_i(\mathbf{x}_1, t_1)g_j(\mathbf{x}_2, t_2)\rangle = K_{ij}\,\delta(\mathbf{x}_1 - \mathbf{x}_2)\,\delta(t_1 - t_2) \tag{2}$$

where K_{ij} is a constant matrix. This form is taken over from that used in the theory of Brownian motion (see, e.g., Ref. 2), where the stochastic source term is indeed a real force, i.e., the fluctuating part of the time derivative of the momentum of a Brownian particle.

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[2] Some authors use the term "Langevin force." Since $g_i(\mathbf{x}, t)$ is dimensionally not a force, we shall eschew this dangerous terminology.

In specifying the statistics of the chemical stochastic source, one should be careful to take account of the nature of the chemical and diffusion processes.

If one considers the case of pure diffusion, with no chemical reaction, then Eq. (1) can be derived from Fick's law and conservation of chemical species.

Considering now the case of only one chemical species, there exists a current $\mathbf{j}$ such that Fick's law takes the form

$$\mathbf{j} = -D\,\nabla\psi + \mathbf{f}_d(\mathbf{x}, t) \tag{3}$$

where $\mathbf{f}_d(\mathbf{x}, t)$ is a stochastic source, which is a vector function, and takes account of the fact that diffusion is a noisy process. However, the conservation law

$$\nabla\cdot\mathbf{j} + (\partial\psi/\partial t) = 0 \tag{4}$$

is by definition *exact*, and does not need stochastic sources. It says simply that, in any small volume, the net number of molecules crossing the boundary gives the net increase in the number of molecules inside the boundary.

Combining (3) and (4) gives an equation like (1), (without a chemical term), with

$$g(\mathbf{x}, t) = -\nabla\cdot\mathbf{f}_d(\mathbf{x}, t) \tag{5}$$

The appropriate correlation function for $\mathbf{f}_d(\mathbf{x}, t)$ is

$$\langle f_{d,i}(\mathbf{x}_1, t_1) f_{d,j}(\mathbf{x}_2, t_2)\rangle = K_d(\mathbf{x}_1, t_1)\,\delta_{ij}\,\delta(\mathbf{x}_1 - \mathbf{x}_2)\,\delta(t_1 - t_2) \tag{6}$$

which says that, at the same point, different components of $\mathbf{j}$ are uncorrelated, which is an assumption, but one which seems very reasonable from the definition (3) of $\mathbf{j}$. Thus (6) and (5) now yield

$$\langle g(\mathbf{x}_1, t_1) g(\mathbf{x}_2, t_2)\rangle = D^2\,\nabla_1\cdot\nabla_2\{K_d(\mathbf{x}_1, t_1)\,\delta(\mathbf{x}_1 - \mathbf{x}_2)\}\,\delta(t_1 - t_2) \tag{7}$$

which is quite a different result from (2).

In the case that there is a chemical reaction as well, a noise term should be added for the chemical part of the process by modifying the conservation law: thus,

$$\frac{\partial\psi}{\partial t} + \nabla\cdot\mathbf{j} = \left.\frac{\partial\psi}{\partial t}\right|_{\text{chem}} + f_c(\mathbf{x}, t) \tag{8}$$

In this case we take the chemical stochastic source $f_c(\mathbf{x}, t)$ to have a correlation function

$$\langle f_c(\mathbf{x}_1, t_1) f_c(\mathbf{x}_2, t_2)\rangle = K_c(\mathbf{x}_1, t_1)\,\delta(\mathbf{x}_1 - \mathbf{x}_2)\,\delta(t_1 - t_2) \tag{9}$$

and we get

$$g(\mathbf{x}, t) = f_c(\mathbf{x}, t) - D\,\nabla\cdot\mathbf{f}_d(\mathbf{x}, t) \tag{10}$$

Assuming that chemical and diffusion sources are uncorrelated, we get

$$\langle g(\mathbf{x}_1, t_1) g(\mathbf{x}_2, t_2)\rangle = \{K_c(\mathbf{x}_1, t_1)\,\delta(\mathbf{x}_1 - \mathbf{x}_2) + D^2\,\nabla_1\cdot\nabla_2[K_d(\mathbf{x}_1, t_1)\,\delta(\mathbf{x}_1 - \mathbf{x}_2)]\}\,\delta(t_1 - t_2) \tag{11}$$

As an example, let us consider the simple reaction given by

$$(\partial\psi/\partial t)|_{\text{chem}} = a - \lambda\psi \tag{12}$$

which corresponds to the reaction

$$A \leftrightarrows X \tag{13}$$

with A held fixed, and ψ representing the concentration of X. We do not have explicit *a priori* knowledge of $K_c(\mathbf{x}, t)$ and $K_d(\mathbf{x}, t)$, but expect them to depend on $\mathbf{x}$ and t only implicitly, through (for example) $\langle\psi(\mathbf{x}, t)\rangle$. Thus, in a steady-state situation, $K_c(\mathbf{x}, t)$ and $K_d(\mathbf{x}, t)$ would be constant. One can calculate the steady-state two-time correlation function

$$\begin{aligned}\mathscr{G}(\mathbf{x}_1 - \mathbf{x}_2, t_1 - t_2) &\equiv \lim_{\substack{t_1\to\infty\\ t_2\to\infty}} \{\langle\psi(\mathbf{x}_1, t_1)\psi(\mathbf{x}_2, t_2)\rangle - \langle\psi(\mathbf{x}_1, t_1)\rangle\langle\psi(\mathbf{x}_2, t_2)\rangle\}\\ &= \frac{1}{(2\pi)^3}\int d^3\mathbf{q}\,\{\exp[i\mathbf{q}\cdot(\mathbf{x}_1 - \mathbf{x}_2)]\}\,\frac{K_c + D^2q^2K_d}{2(Dq^2 + \lambda)}\\ &\quad\times \exp[-(Dq^2 + \lambda)|t_1 - t_2|]\end{aligned} \tag{14}$$

Taking $t_1 = t_2$, we find that if

$$\lambda D K_d = K_c \tag{15}$$

then

$$\mathscr{G}(\mathbf{x}, 0) = (K_c/2\lambda)\,\delta(\mathbf{x}) \tag{16}$$

which corresponds to uncorrelated fluctuations at different spatial points at the same time. This is the result one obtains from the use of master equations(3) to describe chemical reactions.

Any other choice gives a correlation function with correlation length

$$l_c = (D/\lambda)^{1/2} \tag{17}$$

as does the choice of statistics for $g(\mathbf{x}, t)$ of Eq. (2). The Langevin approach is unable to give any other information about $K_c(\mathbf{x}, t)$ and $K_d(\mathbf{x}, t)$ except possibly at equilibrium if statistical mechanical techniques like those used by Einstein(4) for Brownian motion are used.

Van Kampen(5) has recently shown that the use of a stochastic master equation approach, similar to those used in Ref. 3, yields definite predictions for the Langevin forces. By following this method for the reaction (12), one finds an equation of the form (11) does indeed hold, with

$$K_d(\mathbf{x}, t) = 2\langle\psi(\mathbf{x}, t)\rangle/D, \qquad K_c(\mathbf{x}, t) = \lambda\langle\psi(\mathbf{x}, t)\rangle + a \tag{18}$$

so that Eq. (15), though it looks quite arbitrary from a Langevin equation approach, is indeed satisfied in the steady state. Thus, as pointed out in Ref. 3, an equilibrium result of uncorrelated fluctuations at the same time, but different points, is predicted by master equation methods. Furthermore, the result (18) predicts that the variance of ψ is Poissonian, namely if

$$\psi[\Delta V] = \int_{\Delta V} d^3\mathbf{x}\, \psi(\mathbf{x}) \tag{19}$$

then

$$\langle\psi[\Delta V]^2\rangle - \langle\psi[\Delta V]\rangle^2 = \langle\psi[\Delta V]\rangle \tag{20}$$

Only if one *postulates* that the fluctuations are Poissonian and uncorrelated are K_d and K_c in the steady state predicted. Such a postulate cannot, however, in general be made (e.g., see Ref. 3), so that the Langevin equation approach must remain an incomplete theory, unless supplemented by further assumptions, such as the stochastic master equation description adopted by Gardiner *et al.*(3) and van Kampen.(5)

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NOTE ADDED IN PROOF

Grossmann(6) has recently given a very thorough treatment of the problem discussed here, for fluctuations in chemically reacting and hydrodynamic systems.

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