Appearance of correlations and symmetry breaking in non-equilibrium reaction-diffusion systems

LETTER TO THE EDITOR

Appearance of correlations and symmetry breaking in non-equilibrium reaction–diffusion systems

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Abstract. Using the reaction–diffusion master equation of chemical kinetics, we study fluctuations and correlation functions around non-equilibrium steady states. We demonstrate that the underlying Lagrangian description in the Poisson representation possesses in the equilibrium limit an *exact* symmetry which ensures that statistical mechanics is recovered and that the intrinsically non-equilibrium long-range correlations in these systems vanish. An explicit form for the two-time single-particle correlation function, including both the long-range and short-range contributions, is constructed using mean-field arguments.

In recent years many authors have studied the fluctuations and correlation functions for non-equilibrium steady states (Haken 1975, Gardiner *et al* 1976, Lemarchand and Nicolis 1976, Malek Mansour *et al* 1981). Simple fluids near equilibrium have been discussed using kinetic theory and fluctuating hydrodynamics (Ronis *et al* 1979, van der Zwan *et al* 1981, Tremblay *et al* 1981, Kirkpatrick *et al* 1982), while chemical reaction–diffusion models have been described by mean-field (Nitzan *et al* 1974, Gardiner *et al* 1976, Keizer 1982, Nicolis and Malek Mansour 1984, Elderfield and Vvedensky 1985) and renormalisation group (RG) methods (Dewel *et al* 1977, Janssen 1981, Goldhirsch and Procaccia 1981, Vvedensky *et al* 1984, Elderfield and Vvedensky 1985). A major conclusion from these studies is that non-equilibrium constraints lead to long-range correlations which vanish in the equilibrium limit.

In previous papers we have developed a systematic path integral description of reaction–diffusion systems based upon the Poisson transform method introduced by Gardiner and co-workers (Gardiner and Chaturvedi 1977, Gardiner 1983). For the Schlögl (1972) model we applied our approach in the critical regime using RG methods (Elderfield and Vvedensky 1985) and corrected previous attempts at characterising the phase transition (Dewel *et al* 1977, Janssen 1981, Goldhirsh and Procaccia 1981, Vvedensky *et al* 1984). Moreover, we showed that in the equilibrium limit the long-range correlations vanish and statistical mechanics is recovered. This is a general feature of certain reaction–diffusion systems which we show in this letter to result from an exact symmetry of the underlying Lagrangian description of the dynamics in the Poisson representation.

We shall consider the general sequence of R reactions,

$$A_r + N_r X \underset{k_r'}{\overset{k_r}{\rightleftharpoons}} B_r + M_r X \qquad M_r \geq N_r, \quad r = 1, \ldots, R \tag{1}$$
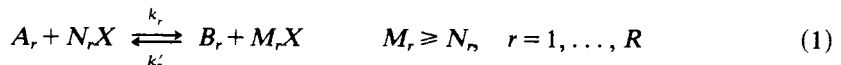
where it is arranged for the concentrations of A_r and B_r, denoted by $[A_r]$ and $[B_r]$, to be held fixed (an open system), while the concentration $[X]$ is monitored. Note that (1) includes the Schlögl (1972) models as special cases. Phenomenologically, the reaction–diffusion master equation associated with (1) is given by the following spatially discrete form (Gardiner 1983):

$$\frac{\partial}{\partial t}P(\{x_i\}, t) = \sum_{i,j=1}^{N} D_{ij}[(x_i+1)P(x_1, \ldots, x_i+1, \ldots, x_j-1, \ldots, x_N, t) - P(\{x_i\}, t)]$$

$$+ \sum_{r=1}^{R}\sum_{i=1}^{N}\left[\kappa_r \frac{(x_i+N_r-M_r)!}{(x_i-M_r)!} P(x_1, \ldots, x_i+N_r-M_r, \ldots, x_N, t) \right.$$

$$+ \kappa_r' \frac{(x_i+M_r-N_r)!}{(x_i-N_r)!} P(x_1, \ldots, x_i+M_r-N_r, \ldots, x_N, t)$$

$$\left. - \left(\kappa_r \frac{x_i!}{(x_i-N_r)!} + \kappa_r' \frac{x_i!}{(x_i-M_r)!} \right) P(\{x_i\}, t) \right] \tag{2}$$

where $\kappa_r = k_r[A_r]$, $\kappa_r' = k_r'[B_r]$, x_i is the number of X molecules in the ith cell, the non-local terms represent cell-to-cell diffusion and the local terms are specified by the reaction sequence (1). Several schemes have been developed for converting the master equation (2) into the more computationally suitable form of a Fokker–Planck equation. However, only the Poisson representation yields a Fokker–Planck equation *exactly* equivalent to (2) both near and far from equilibrium. Accordingly, to solve (2) we write P as a superposition of Poissonians (Gardiner and Chaturvedi 1977, Gardiner 1983):

$$P(\{x_i\}, t) = \int_{\mathscr{C}} \prod_{i=1}^{N} \left(d\mu(\alpha_i) \frac{\exp(-\alpha_i)\alpha_i^{x_i}}{x_i!} \right) f(\{\alpha_i\}, t) \tag{3}$$

where $\mathscr{C}$ is a closed contour in the complex plane and as such f is best viewed as a Markovian quasiprobability. Substituting (3) into (2) we find that the Poissonian fluctuations are described exactly by the Fokker–Planck equation

$$\frac{\partial}{\partial t}f(\{\alpha_i\}, t) = - \sum_{i,j=1}^{N} \frac{\partial}{\partial \alpha_i} D_{ij}\alpha_j f(\{\alpha_i\}, t)$$

$$+ \sum_{r=1}^{R}\sum_{i=1}^{N} \left[\left(1-\frac{\partial}{\partial \alpha_i}\right)^{M_r} - \left(1-\frac{\partial}{\partial \alpha_i}\right)^{N_r} \right] (\kappa_r\alpha_i^{N_r} - \kappa_r'\alpha_i^{M_r}) f(\{\alpha_i\}, t). \tag{4}$$

Denoting averages in the concentration and Poisson representations by $\langle\!\langle \ \rangle\!\rangle$ and $\langle \ \rangle$, respectively, we find that equal-time correlation functions are related by the connection formula

$$\left\langle\!\!\!\left\langle \frac{x_i!}{(x_i-p)!} \frac{x_j!}{(x_j-q)!} \cdots \right\rangle\!\!\!\right\rangle \overset{i\neq j\neq\ldots}{=} (\alpha_i^p\alpha_j^q \ldots) \tag{5}$$

or, more explicitly,

$$\langle\!\langle x_i \rangle\!\rangle = \langle \alpha \rangle$$
$$\langle\!\langle x_i x_j \rangle\!\rangle = \langle \alpha_i\alpha_j \rangle + \delta_{ij}\langle \alpha_i \rangle. \tag{6}$$

The extension of (5) and (6) to multi-time correlation and response functions has been described recently by Elderfield (1985) (see below).

We represent the solution of (4) in the form of a functional integral using a variant of the Martin-Siggia-Rose (MSR) formalism (Martin *et al* 1973) and obtain the generating functional Z for Poissonian correlation and response functions as (Elderfield 1985)

$$Z(l, \hat{l}) = \int [\mathrm{d}\alpha][\mathrm{d}\hat{\alpha}] \exp\left(\int \mathrm{d}t(L + l\alpha + \hat{l}\hat{\alpha})\right) \tag{7}$$

where the Lagrangian L takes the form

$$L = \sum_{p,q=1}^{N} \mathrm{i}\alpha_p(t)\left(-D_{pq} + \delta_{pq}\frac{\partial}{\partial t}\right)\alpha_q(t)$$

$$+ \sum_{r=1}^{R}\sum_{p=1}^{N} [(1 - \mathrm{i}\hat{\alpha}_p(t))^{M_r} - (1 - \mathrm{i}\hat{\alpha}_p(t))^{N_r}][\kappa_r\alpha_p^{N_r}(t) - \kappa_r'\alpha_p^{M_r}(t)]. \tag{8}$$

As usual one has

$$\langle \alpha_i(t)\rangle = \frac{\partial}{\partial l_i(t)} Z(l, \hat{l})|_{l=\hat{l}=0}$$

$$\langle \hat{\alpha}_i(t)\alpha_j(t')\rangle = \mathrm{i}\frac{\partial}{\partial h_i(t)}\langle \alpha_j(t')\rangle = \frac{\partial^2 Z(l, \hat{l})}{\partial l_i(t)\,\partial l_j(t')}\bigg|_{l=\hat{l}=0} \tag{9}$$

with their natural generalisations. Moreover, within this framework the connection formula for the two-time correlation function takes the form (Elderfield 1985)

$$\langle\!\langle x_p(t)x_q(t')\rangle\!\rangle \overset{t>t'}{=} \langle \alpha_p(t)\alpha_q(t')\rangle + \mathrm{i}\langle \alpha_q(t)\alpha_q(t')\hat{\alpha}_q(t')\rangle \tag{10}$$

which in the limit $t \to t'$ reduces to the second of equations (6). Readers familiar with the MSR formalism will observe that our Lagrangian contains no Jacobian term, since we have defined

$$\langle \hat{\alpha}_i^p(t)\alpha_j^q(t)\rangle = 0 \tag{11}$$

for $p > 1$ and all q.

We may recast (4) in the form of a Langevin equation by first writing (8) in the more conventional form

$$L = \sum_{p,q=1}^{N} \mathrm{i}\alpha_p(t)\left(-D_{pq}\alpha_q(t) + \delta_{pq}\frac{\partial\alpha_p(t)}{\partial t}\right.$$

$$\left. - \delta_{pq}\sum_{r=1}^{R}(M_r - N_r)[\kappa_r\alpha_p^{N_r}(t) - \kappa_r'\alpha_p^{M_r}(t)]\right) + \sum_{p=1}^{N}\sum_{n=2}^{\max\{M_r\}}\frac{(-1)^n}{n!}(\mathrm{i}\alpha_p(t))^n$$

$$\times \left[\sum_{r=1}^{R}\left(\frac{M_r!}{(M_r-n)!} - \frac{N_r!}{(N_r-n)!}\right)[\kappa_r\alpha_p^{N_r}(t) - \kappa_r'\alpha_p^{M_r}(t)]\right] \tag{12}$$

where we take negative factorials to vanish. Conversion to a Langevin equation is now straightforward and we obtain the *multiplicative* form

$$\frac{\partial\alpha_p(t)}{\partial t} = \sum_{q=1}^{N} D_{pq}\alpha_q(t) + \sum_{r=1}^{R}(M_r - N_r)[\kappa_r\alpha_p^{N_r}(t) - \kappa_r'\alpha_p^{M_r}(t)]$$

$$+ \sum_{n=1}^{\max\{M_r\}}\left[\sum_{r=1}^{R}\left(\frac{M_r!}{(M_r-n)!} - \frac{N_r!}{(N_r-n)!}\right)[\kappa_r\alpha_p^{N_r}(t) - \kappa_r'\alpha_p^{M_r}(t)]\right]^{1/n}\xi_p^{(n)}(t) \tag{13}$$

where $\xi^{(n)}$ is an nth-order δ-corrected noise, i.e.

$$\langle \xi^{(n)}_{p_1}(t_1) \ldots \xi^{(n)}_{p_n}(t_n)\rangle = \delta_{p_1,p_2} \ldots \delta_{p_{n-1},p_n} \delta(t_1 - t_2) \ldots \delta(t_{n-1} - t_n) \qquad (14)$$

with all lower-order moments vanishing and an Ito interpretation of (13) is to be understood.

In order to achieve a steady state in the reaction scheme (1), the $[A_r]$ and $[B_r]$ must be adjusted at rates R_r given by

$$R_r = \kappa_r[X]^{N_r} - \kappa'_r[X]^{M_r} \qquad (15)$$

so true equilibrium (no fluxes, $R = 0$) occurs only if each reaction balances independently (detailed balance):

$$\kappa_r[X]^{N_r} = \kappa'_r[X]^{M_r}. \qquad (16)$$

Guided by this observation, we consider the symmetries of the Lagrangian (8) and (12) under the constraints

$$\kappa_r/\kappa'_r = \lambda^{M_r - N_r} \qquad (17)$$

where λ is a constant. Given (17) and (8) a little algebra uncovers the invariance of the Lagrangian under the interchange

$$i\hat{\alpha}(t) \rightleftharpoons (1/\lambda)[\lambda - \alpha(-t)] \qquad (18)$$

from which we obtain

$$\begin{aligned}
\langle \alpha(t)\rangle &= \lambda\langle 1 - i\hat{\alpha}(-t)\rangle = \lambda \\
\langle \alpha(t)\alpha(t)\rangle - \langle \alpha(t)\rangle^2 &= \lambda^2\langle i\hat{\alpha}(-t)i\hat{\alpha}(-t)\rangle = 0
\end{aligned} \qquad (19)$$

since $\langle(\hat{\alpha})^p\rangle = 0$, as is easily demonstrated (de Dominicis and Peliti 1978). From (19) we infer that the fluctuations are suppressed by (17) and, moreover, using the connection formula (6), $\langle \alpha\rangle = \langle\!\langle x\rangle\!\rangle$, we deduce that the constraint (17) is nothing other than the detailed balance condition (16). In equilibrium the Poissonian fluctuations are suppressed and one finds the stationary distribution

$$P_S(\{x_i\}) = \prod_{i=1}^{N} \frac{e^{-\alpha}\alpha^{x_i}}{x_i!} \qquad (20)$$

in full agreement with statistical mechanics (Landau and Lifschitz 1959).

To describe true non-equilibrium steady states or temporal correlations one must resort to approximate methods. We consider the mean-field or Gaussian approximation to (7) and (12) and define the density $\rho = \langle\!\langle x_i\rangle\!\rangle/V$, $V \to 0$, to satisfy the deterministic equation in the continuum limit ($D_{ij} \to \nabla^2$, $v_r = \kappa_r V^{N_r-1}$, $v'_r = \kappa'_r V^{M_r-1}$):

$$\sum_{r=1}^{R} (M_r - N_r)(v_r\rho^{N_r} - v'_r\rho^{M_r}) = 0. \qquad (21)$$

Introducing the correlation length ξ and current J,

$$\begin{aligned}
\xi &= \left(\frac{1}{D}\frac{\partial}{\partial\rho}\sum_r (M_r - N_r)(v_r\rho^{N_r} - v'_r\rho^{M_r})\right)^{-1/2} \\
J &= \tfrac{1}{2}\sum_r [M_r(M_r - 1) - N_r(N_r - 1)](v_r\rho^{N_r} - v'_r\rho^{M_r})
\end{aligned} \qquad (22)$$

we find in the continuum limit that the correlation function $C(q, \omega)$, defined to be

$$C(q\omega) = \delta(q - q') \, \delta(\omega - \omega')[\langle\!\langle\rho(q\omega)\rho(q'\omega')\rangle\!\rangle - \langle\!\langle\rho(q\omega)\rangle\!\rangle^2(2\pi)^{d+1} \, \delta(q) \, \delta(\omega)] \qquad (23)$$

is given by

$$C(q\omega) = \delta(q - q') \, \delta(\omega - \omega')\left(\frac{2J}{[D(q^2 + \xi^{-2})]^2 + \omega^2} + \left(\frac{\rho}{D(q^2 + \xi^{-2}) + i\omega} + \text{cc}\right)\right). \qquad (24)$$

Fourier transforming we obtain

$$C(rt; r't') = \frac{J}{4\pi D|r - r'|} \exp\left(-\frac{|r - r'|}{\xi}\right)$$
$$+ \rho\left(\frac{1}{4\pi D(t - t')}\right)^{3/2} \exp\left[-\left(\frac{|r - r'|^2}{4D(t - t')} + \frac{D(t - t')}{\xi^2}\right)\right] \qquad (25)$$

where in equilibrium (cf (16)) the first (or long-range) term vanishes identically as discussed above. Consequently, at short times the equilibrium correlations are intrinsically short-ranged:

$$C_{eq}(rt; r'0) = \rho\left(\frac{1}{4\pi Dt}\right)^{3/2} \exp\left[-\left(\frac{|r - r'|^2}{4Dt} + \frac{Dt}{\xi^2}\right)\right] \xrightarrow{t \to 0} \rho \, \delta(r - r'). \qquad (26)$$

Simple mean-field approximations thus yield the full two-time correlation function, including both the short- and long-range contribution. In the equal-time limit (25) reduces to the expression.

$$C(rt; r't) = \frac{J}{4\pi D|r - r'|} \exp\left(-\frac{|r - r'|}{\xi}\right) + \rho \, \delta(r - r') \qquad (27)$$

obtained previously by other authors (Gardiner and Chaturvedi 1977, Keizer 1982, Nicolis and Malek Mansour 1984, Vvedensky *et al* 1984).

To summarise, we have shown using the Poisson representation of the reaction-diffusion master equation that the recovery of statistical mechanics in equilibrium results from an exact symmetry of the underlying Lagrangian. The two-point correlation function was derived in mean-field theory to explicitly demonstrate the decay of non-equilibrium correlations as the external constraints are relaxed. Of course, the symmetry (18) does not provide a very stringent constraint on the Gaussian approximation to the Lagrangian (8), though failure to respect the symmetry in the non-linear terms may lead not only to the loss of the correct equilibrium limit, but to an erroneous characterisation of the non-linear behaviour of the system as well (Janssen 1981, Elderfield and Vvedensky 1985). Indeed, since the associated Langevin equation (13) is *multiplicative*, we expect qualitative differences to result beyond mean-field theory by replacing (13) with additive or pseudo-additive dynamics.

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