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Exact macroscopic dynamics in non-equilibrium chemical systems

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Abstract. Non-equilibrium reaction–diffusion models show an exciting array of critical phenomena, ranging from the continuous transitions reminiscent of equilibrium systems to the spectacular chemical oscillators. Transforming the underlying stochastic master equations using ‘Poisson’ techniques we obtain for the first time a comprehensive description of the dynamics, including in particular the problematical multitime correlation functions. Our formalism is ideally adapted for the use of scaling and renormalisation group ideas.

1. Introduction

In recent years non-equilibrium phase transitions have been studied in great depth (Haken 1975, Nicolis and Prigogine 1977). Chemical reaction–diffusion models in particular show an exciting array of critical phenomena. For example the Schlögl (1972) models exhibit both continuous and discontinuous transitions reminiscent of equilibrium systems, whilst the Brusselator (Glansdorff and Prigogine 1971) is probably the simplest example of a chemical oscillator.

Two complementary approaches to the physics of these systems are apparent in the literature. Many authors (Nitzan *et al* 1974, Keizer 1976) have advocated simple phenomenological Langevin or Fokker Planck descriptions; however, in direct contrast to equilibrium studies both the structure of the stationary distribution functions and the associated fluctuation–dissipation theorems are in general unknown, so these often represent an unwarranted extrapolation from some underlying deterministic approximation. The Schlögl model is in fact a prime example, for this system is driven by a rather curious multiplicative noise (Vvedensky *et al* 1984).

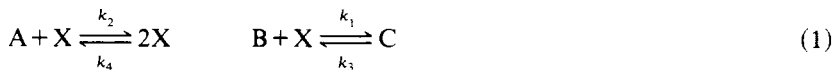
An alternative scheme is provided by the stochastic master equations described by Chaturvedi *et al* (1977), van Kampen (1976) and Nicolis and Prigogine (1971), which are based on the simplest kinetic picture of reactions mediated by collisions and particles moving about in space by diffusion. A direct linearisation of these equations shows that the phenomenological approach can be seriously in error as noted above; however, it is also practically impossible to obtain systematic approximations in the vicinity of the phase transitions (van Kampen 1976, McQuarrie 1967, Kubo 1962). The exception to this rule is the work of Gardiner and Chaturvedi (1977) (to be referred to as GC) who presented the ‘Poisson transformation’, via which the *exact* Fokker Planck or Langevin description could be derived from these master equations. Unhappily there was a major drawback to this approach in that only the *equal* time correlation functions for the chemical fluctuations were readily accessible, the *unequal*

time functions again only being obtainable within the linear (or Gaussian) approximation (Chaturvedi *et al* 1977, Gardiner and Chaturvedi 1978). In this paper we remedy this weakness, obtaining for the first time a complete dynamical description for these interesting non-equilibrium systems. Using our formalism we can generate simple dynamical equations of state which contain all the correlation/response information, but for which *no* underlying static thermodynamic description (based on the familiar state functions such as entropy) exists. One is thus led to a generalised thermodynamical description as recently conjectured by Nicolis and Malek Mansour (1984). In particular, we can study the local/global stability criteria associated with such descriptions (Luo Jiu *et al* 1984). Further, for these non-equilibrium chemical systems it has often been observed (in mean field theory—Walgraef *et al* 1982, Gardiner 1983) that there is a natural dichotomy between long and short range correlations, the former apparently vanishing in the equilibrium limit (Nicolis and Malek Mansour 1984). The Poisson representation describes this feature in a very simple way (Elderfield and Vvedensky 1984); indeed, the $\alpha(\mathbf{r}, t)$ variables are precisely those coordinates whose existence was recently conjectured (Prigogine and George 1983).

Finally, we would observe that for these systems, scaling and renormalisation group ideas have not yet been systematically applied, due principally to the lack of a simple, dynamical Landau-Ginzburg description. Our description, obtained essentially from first principles, is precisely of this form, so we are in an ideal position to extend, simplify and *correct* all previous studies (Dewel *et al* 1977, Goldhirsch and Procaccia 1981, Janssen 1981, Vvedensky *et al* 1984). As one would expect, the existence of dominant multiplicative noises or the absence of simple potential solutions (Gardiner 1983) leads to the identification of universality classes not seen in equilibrium studies. We shall here illustrate the Poisson formalism using the Schlögl model, reserving a complete study and extensions to treat, for example, the Brusselator to future communications.

2. The Poisson formalism

The simplest stochastic master equation for chemical reaction-diffusion systems is provided by the Schlögl (1972) model defined by the reactions



where it is arranged for the concentrations of A, B and C to be held fixed (an open system) whilst the concentration of X is monitored. Phenomenologically the master equation is defined (GC) by the following spatially discrete form:

$$\begin{aligned} \frac{\partial}{\partial t} P(\{x_i\}, t) = & \sum_{i,j}^N D_{ij} [(x_i + 1)P(x_1, \dots, x_i + 1, \dots, x_j - 1, \dots, x_N, t) - P(\{x_i\}, t)] \\ & + \sum_{i=1}^N \{k_1 B(x_i + 1)P(x_1, \dots, x_i + 1, \dots, x_N, t) \\ & + k_3 C P(x_1, \dots, x_i - 1, \dots, x_N, t) \\ & + k_2 A(x_i - 1)P(x_1, \dots, x_i - 1, \dots, x_N, t) \\ & + k_4(x_i + 1)x_i P(x_1, \dots, x_i + 1, \dots, x_N, t) \\ & - [k_1 Bx_i + k_3 C + k_2 Ax_i + k_4 x_i(x_i - 1)]P(\{x_i\}, t)\}. \end{aligned} \quad (2)$$

Here x_i is the number of X molecules in the i th cell. As one would expect, the first term represents the cell-to-cell diffusion, whilst the second specifies the chemical reaction (1).

To solve (2), GC proposed writing the distribution P as a superposition of Poissonians

$$P(\{x_i\}, t) = \int_{\mathcal{D}} \prod_{i=1}^N \left(d\mu(\alpha_i) \frac{[\exp(\alpha_i)](\alpha_i)^{x_i}}{(x_i)!} \right) f(\{\alpha_i\}, t). \tag{3}$$

Observe that f need not be positive, so it is best viewed as a Markovian quasiprobability. For clarity we shall treat only the real Poisson representation (RP) ($d\mu(\alpha) = d\alpha$, $\mathcal{D} \subset \mathcal{R}$); however, the complex Poisson and positive Poisson cases described by Gardiner (1983) offer no additional problems. Introducing equation (3), (RP) into equation (1) and integrating by parts, one finds, on dropping the boundary terms, that $f(\{\alpha_i\}, t)$ satisfies the following Fokker Planck equation:

$$\begin{aligned} \frac{\partial}{\partial t} f(\{\alpha_i\}, t) = & - \sum_{i=1}^N \frac{\partial}{\partial \alpha_i} \left[\left(\sum_{j=1}^N D_{ij} \alpha_j + k_3 C + (k_2 A - k_1 B) \alpha_i - k_4 \alpha_i^2 \right) f(\{\alpha_i\}, t) \right. \\ & \left. + \sum_{i=1}^N \frac{\partial^2}{\partial \alpha_i^2} (k_2 A \alpha_i - k_4 \alpha_i^2) f(\{\alpha_i\}, t) \right]. \end{aligned} \tag{4}$$

The strength of the Poisson transformation as an analytic tool lies in two notable features; (i) it is *exact*; and (ii) the spatial diffusion appears only in the drift term of the Fokker Planck equation. No other approach offers these advantages; cumulant expansions inevitably are simply truncated, whilst Kramers-Moyal techniques lead to Fokker Planck equations with both non-local diffusion and drift. In addition, from (4) it follows directly that the underlying Langevin equation may be written in the *exact* form

$$\begin{aligned} \frac{d\alpha_i}{dt} = & \sum_{j=1}^N D_{ij} \alpha_j + [k_3 C + (k_2 A - k_1 B) \alpha_i - k_4 \alpha_i^2] + [2\alpha_i (k_2 A - k_4 \alpha_i)]^{1/2} \xi_i(t) \\ \langle \xi_i(t) \xi_j(t') \rangle = & \delta_{ij} \delta(t - t') \end{aligned} \tag{5}$$

where we have used the Ito prescription for the noise.

Together, (4) and (5) present a very flexible framework for computing the Poissonian dynamics; however, there is a drawback. Let us consider for a moment the relation between chemical and Poissonian fluctuations. For *equal* time correlations it is obvious from (3) that

$$\left\langle \left\langle \frac{(x_i)!}{(x_i - p)!} \frac{(x_j)!}{(x_j - k)!} \dots \right\rangle \right\rangle \stackrel{i \neq j \dots}{=} \langle (\alpha_i)^p (\alpha_j)^k \dots \rangle \tag{6}$$

or more explicitly

$$\begin{aligned} \langle \langle x_i \rangle \rangle &= \langle \alpha_i \rangle \\ \langle \langle x_i x_j \rangle \rangle &= \langle \alpha_i \alpha_j \rangle + \delta_{ij} \langle \alpha_i \rangle \\ &\vdots \qquad \qquad \qquad \vdots \end{aligned} \tag{7}$$

To obtain *multitime* information about the chemical fluctuations is far more difficult, as we will see below. However, it is clearly of great importance to obtain the generalisation of (6) to *unequal* times, unlocking the wealth of information hidden in (4) and (5).

For clarity we shall tackle the problem in simple stages. Firstly we shall suppress the spatial diffusion and study the Poissonian Fokker Planck equation

$$\frac{\partial}{\partial t} f(\alpha, t) = \frac{\partial}{\partial \alpha} \left(A(\alpha) f(\alpha, t) + \frac{\partial}{\partial \alpha} (B(\alpha) f(\alpha, t)) \right) \tag{8}$$

where $A(\alpha)$ and $B(\alpha)$ are defined as follows:

$$\begin{aligned} A(\alpha) &= -[k_3 C + (k_2 A - k_1 B)\alpha - k_4 \alpha^2] \\ B(\alpha) &= (k_2 A - k_4 \alpha)\alpha. \end{aligned} \tag{9}$$

Now it is useful to associate with (8) a quantum problem, described by a Hamiltonian \hat{H}

$$\hat{H} = \hat{p}(A(\hat{\alpha}) - i\hat{p}B(\hat{\alpha})) \tag{10}$$

where the operators \hat{p} and $\hat{\alpha}$ satisfy the familiar commutation rules

$$[\hat{p}, \hat{\alpha}] = i \quad [\hat{p}, \hat{p}] = 0 = [\hat{\alpha}, \hat{\alpha}] \tag{11}$$

On introducing the evolution operator $\hat{U}(t, t_0)$ defined by the relations

$$\begin{aligned} i \frac{\partial}{\partial t} \hat{U}(t, t_0) &= \hat{H}(\hat{p}, \hat{\alpha}) \hat{U}(t, t_0) \\ \hat{U}(t_0, t_0) &= \hat{I} \end{aligned} \tag{12}$$

we may then solve (8) in the form

$$f(\alpha, t | \alpha_0, t_0) = \langle \alpha | \hat{U}(t, t_0) | \alpha_0 \rangle \tag{13}$$

with the initial condition

$$f(\alpha, t_0 | \alpha_0, t_0) = \delta(\alpha - \alpha_0) \tag{14}$$

and where we use the usual notation for bras and kets: $\hat{\alpha}|\alpha\rangle = \alpha|\alpha\rangle$, $\hat{p}|p\rangle = p|p\rangle$, $\langle \alpha | \alpha' \rangle = \delta(\alpha - \alpha')$, $\langle p | \alpha \rangle = (1/2\pi) \exp(ip\alpha)$. Pursuing the analogy a little further, it is natural to introduce the Heisenberg operators $\hat{\alpha}(t)$ and $\hat{p}(t)$, satisfying the equations of motion

$$\begin{aligned} \frac{d}{dt} \hat{\alpha}(t) &\equiv i[\hat{H}(\hat{p}(t), \hat{\alpha}(t)), \hat{\alpha}(t)] = -A(\hat{\alpha}(t)) + 2i\hat{p}(t)B(\hat{\alpha}(t)) \\ \frac{d}{dt} \hat{p}(t) &\equiv i[\hat{H}(\hat{p}(t), \hat{\alpha}(t)), \hat{p}(t)] = -\hat{p}(t) \frac{\partial A(\hat{\alpha}(t))}{\partial \hat{\alpha}(t)} - i(\hat{p}(t))^2 \frac{\partial B(\hat{\alpha}(t))}{\partial \hat{\alpha}(t)} \end{aligned} \tag{15}$$

and in terms of which multitime Poisson averages can be expressed using standard techniques (see Feynman and Hibbs 1965, Faddeev 1975). For example

$$\langle \alpha(t_1) \alpha(t_2) \dots \alpha(t_k) \rangle_{\alpha_0} = \int d\alpha \langle \alpha | T(\hat{\alpha}(t_1) \hat{\alpha}(t_2) \dots \hat{\alpha}(t_k)) | \alpha_0 \rangle \tag{16}$$

where T is the time-ordering operator (latest times to the left) and we have made explicit the initial condition $\alpha = \alpha_0$ at $t = t_0$.

With this background we can now show how to interpret the two point Poisson correlation function

$$\langle \alpha(t)\alpha(t') \rangle_{\alpha_0}^{t > t'} = \int d\alpha d\alpha' \alpha \alpha' f(\alpha, t | \alpha', t') f(\alpha', t' | \alpha_0, t_0) \tag{17}$$

in terms of chemical correlations. Now the defining master equation is Markovian, so it follows directly that the conditional Poisson distribution $f(\alpha, t | \alpha_0, t_0)$ and the chemical distribution $P(x, t | x_0, t_0)$ are related by the important identity

$$\sum_{x, x'} \frac{x!}{(x-p)!} P(x, t | x', t') \frac{[\exp(-\alpha')](\alpha')^{x'}}{(x')!} = \int d\alpha \alpha^p f(\alpha, t | \alpha', t'). \tag{18}$$

Using the relation repeatedly we may rewrite (17) in the form

$$\begin{aligned} \langle \alpha(t)\alpha(t') \rangle_{\alpha_0}^{t > t'} &= \sum_{x, x'=0}^{\infty} \int d\alpha x P(x, t | x', t') \frac{[\exp(-\alpha')](\alpha')^{x'+1}}{(x')!} f(\alpha', t' | \alpha_0, t_0) \\ &= \sum_{x, x'=0}^{\infty} \int d\alpha x P(x, t | x', t') \left[\left(-\alpha' \frac{\partial}{\partial \alpha'} + x' \right) \frac{[\exp(-\alpha')](\alpha')^{x'}}{(x')!} \right] f(\alpha', t' | \alpha_0, t_0) \\ &= \langle\langle x(t)x(t') \rangle\rangle_{\alpha_0} + \int d\alpha d\alpha' \alpha f(\alpha, t | \alpha', t') \left(\frac{\partial}{\partial \alpha'} [\alpha' f(\alpha', t' | \alpha_0, t_0)] \right), \end{aligned} \tag{19}$$

derived originally by Gardiner and Chaturvedi (1978). In terms of the quantum analogue the new term appearing on the right hand side is easily interpreted, so we obtain

$$\langle\langle x(t)x(t') \rangle\rangle_{\alpha_0}^{t > t'} = \int d\alpha \langle \alpha | (\hat{\alpha}(t)\hat{\alpha}(t') + i\hat{\alpha}(t)\hat{p}(t')\hat{\alpha}(t')) | \alpha_0 \rangle. \tag{20}$$

Observe that in the equal time limit $t \rightarrow t'$, (20) reproduces the known expression (7), for causality ensures

$$\int d\alpha \langle \alpha | \hat{p}(t) = \hat{0}. \tag{21}$$

Higher correlation functions follow in a similar manner, for example using the fundamental relation (18) one finds

$$\begin{aligned} \langle \alpha(t)\alpha(t')\alpha(t'') \rangle_{\alpha_0}^{t > t' > t''} &= \int d\alpha d\alpha' d\alpha'' \alpha \alpha' \alpha'' f(\alpha, t | \alpha', t') f(\alpha', t' | \alpha'', t'') f(\alpha'', t'' | \alpha_0, t_0) \\ &= \sum_{x, x'=0}^{\infty} \int d\alpha' d\alpha'' x P(x, t | x', t') \\ &\quad \times \frac{[\exp(-\alpha')](\alpha')^{x'+1}}{(x')!} f(\alpha', t' | \alpha'', t'') f(\alpha'', t'' | \alpha_0, t_0) \\ &= \sum_{x, x', x''=0}^{\infty} \int d\alpha'' x x' P(x, t | x', t') P(x', t' | x'', t'') \\ &\quad \times \frac{[\exp(-\alpha'')](\alpha'')^{x''+1}}{(x'')!} f(\alpha'', t'' | \alpha_0, t_0) \end{aligned}$$

$$\begin{aligned}
 &= \sum_{x,x',x''=0}^{\infty} \int d\alpha'' \, x x' P(x, t | x', t') P(x', t' | x'', t'') \left[\left(-\alpha'' \frac{\partial}{\partial \alpha''} + x'' \right) \right. \\
 &\quad \times \left. \frac{[\exp(-\alpha'')](\alpha'')^{x''+1}}{(x'')!} \right] f(\alpha'', t'' | \alpha_0, t_0) \\
 &= \langle\langle x(t)x(t')x(t'') \rangle\rangle_{\alpha_0} \\
 &\quad + \int d\alpha \, d\alpha' \, d\alpha'' \, \alpha f(\alpha, t | \alpha', t') \alpha' f(\alpha', t' | \alpha'', t'') \left(\frac{\partial}{\partial \alpha''} [\alpha'' f(\alpha'', t'' | \alpha_0, t_0)] \right)
 \end{aligned}$$

which may be interpreted in terms of the quantum analogue as

$$\langle\langle x(t)x(t')x(t'') \rangle\rangle_{\alpha_0} \stackrel{t > t' > t''}{=} \int d\alpha \langle \alpha | (\hat{\alpha}(t)\hat{\alpha}(t')\hat{\alpha}(t'') + i\hat{\alpha}(t)\hat{\alpha}(t')\hat{p}(t'')\hat{\alpha}(t'')) | \alpha_0 \rangle. \tag{22}$$

For completeness it is also useful to analyse another three point multitime correlation function

$$\begin{aligned}
 \langle \alpha(t)(\alpha(t'))^2 \rangle_{\alpha_0} &\stackrel{t > t'}{=} \int d\alpha \, d\alpha' \, \alpha (\alpha')^2 f(\alpha, t | \alpha', t') f(\alpha', t' | \alpha_0, t_0) \\
 &= \sum_{x,x'=0}^{\infty} \int d\alpha' \, x P(x, t | x', t') \frac{[\exp(-\alpha')](\alpha')^{x+2}}{(x')!} f(\alpha', t' | \alpha_0, t_0) \\
 &= \sum_{x,x'=0}^{\infty} \int d\alpha' \, x P(x, t | x', t') \left[\left(-\alpha' \frac{\partial}{\partial \alpha'} + x' + 1 \right) \right. \\
 &\quad \times \left. \left(-\alpha' \frac{\partial}{\partial \alpha'} + x' \right) \frac{[\exp(-\alpha')](\alpha')^{x'}}{(x')!} \right] f(\alpha', t' | \alpha_0, t_0) \\
 &= \langle\langle x(t)x(t')(x(t')+1) \rangle\rangle_{\alpha_0} \\
 &\quad + \int d\alpha \, d\alpha' \, \alpha f(\alpha, t | \alpha', t') \left\{ \frac{\partial}{\partial \alpha'} \left[\alpha' \left(\frac{\partial}{\partial \alpha'} [\alpha' f(\alpha', t' | \alpha_0, t_0)] \right) \right] \right\} \\
 &\quad + \sum_{x,x'} \int d\alpha' \, x P(x, t | x', t') \left[\left(2\alpha' \frac{\partial}{\partial \alpha'} + 1 \right) \frac{(\alpha')^{x'}}{(x')!} \right. \\
 &\quad \times \left. [\exp(-\alpha')] \frac{\partial}{\partial \alpha'} [\alpha' f(\alpha', t' | \alpha_0, t_0)] \right] \\
 &= \langle\langle x(t)x(t')(x(t')-1) \rangle\rangle_{\alpha_0} \\
 &\quad + \int d\alpha \, d\alpha' \, \alpha f(\alpha, t | \alpha', t') \\
 &\quad \times \left(\frac{\partial}{\partial \alpha'} (2\alpha' f(\alpha', t' | \alpha_0, t_0)) - \frac{\partial}{\partial \alpha'} [(\alpha')^2 f(\alpha', t' | \alpha_0, t_0)] \right)
 \end{aligned}$$

which can be interpreted in the form

$$\begin{aligned}
 &\langle\langle x(t)x(t')(x(t')-1) \rangle\rangle_{\alpha_0} \\
 &\stackrel{t > t'}{=} \int d\alpha \langle \alpha | (\hat{\alpha}(t)(\hat{\alpha}(t'))^2 + 2i\hat{\alpha}(t)\hat{p}(t')(\hat{\alpha}(t')^2) \\
 &\quad - \hat{\alpha}(t)(\hat{p}(t'))^2(\hat{\alpha}(t')^2) | \alpha_0 \rangle. \tag{23}
 \end{aligned}$$

Now, to reintroduce spatial diffusion into the problem it is helpful to reformulate our quantum mechanical expressions in terms of functional integrals. Consider for example the distribution $f(\alpha, t_f | \alpha_0, t_0)$, then dividing the interval (t_0, t_f) by points $t_k = t_0 + k\varepsilon$, $(n + 1)\varepsilon = t_f - t_0 > 0$, $t_{n+1} = t_f$ one may write the familiar steps

$$\begin{aligned}
 f(\alpha_f, t_f | \alpha_0, t_0) &= \langle \alpha_f | \hat{V}(t_f, t_0) | \alpha_0 \rangle \\
 &= \lim_{n \rightarrow \infty} \left(\int \prod_{i=1}^n d\alpha_i \prod_{j=1}^{n+1} \langle \alpha_j | \hat{U}(t_j, t_{j-1}) | \alpha_{j-1} \rangle \right) \\
 &= \lim_{n \rightarrow \infty} \left[\int \prod_{i=1}^n d\alpha_i \prod_{j=1}^{n+1} \frac{dp_j}{(2\pi)^{1/2}} \exp \left\{ -i\varepsilon \left[\sum_{k=1}^n p_k \left(\frac{\alpha_k - \alpha_{k-1}}{\varepsilon} \right) \right. \right. \right. \\
 &\quad \left. \left. \left. + A(\alpha_{k-1}) - ip_k B(\alpha_{k-1}) \right) \right] \right] \\
 &\equiv \int [d\alpha(t)] \int [dp(t)] \delta(\alpha(t_0) - \alpha_0) \delta(\alpha(t_f) - \alpha_f) \exp \left(-i \int_{t_0}^{t_f} dt \mathcal{L} \right) \quad (24)
 \end{aligned}$$

with the Lagrangian

$$\mathcal{L} = p(t)(\dot{\alpha}(t) + A(\alpha(t)) - ip(t)B(\alpha(t))). \quad (25)$$

In the same way multitime correlation functions can be expressed in the form

$$\begin{aligned}
 \langle \alpha_f | T(\hat{\alpha}(t_1) \dots \hat{\alpha}(t_k) \hat{p}(t'_1) \dots \hat{p}(t'_l)) | \alpha_0 \rangle \\
 = \int [d\alpha(t)] \int [dp(t)] \alpha(t_1) \dots \alpha(t_k) p(t'_1) \dots p(t'_l) \\
 \times \left[\delta(\alpha(t_f) - \alpha_f) \delta(\alpha(t_0) - \alpha_0) \exp \left(-i \int_{t_0}^{t_f} dt \mathcal{L} \right) \right]. \quad (26)
 \end{aligned}$$

Providing all the time arguments $(t_1, t_2, \dots, t_k, t'_1, t'_2, \dots, t'_l)$ in (26) are distinct, this argument is perfectly adequate. Our problem, however, involves the composite operator $\hat{p}\hat{\alpha}(t)$ (see (20)), so we must be more careful. Working in the above discretisation, we find typically that

$$\begin{aligned}
 \langle G(p(t))F(\alpha(t)) \rangle_{\alpha_0} &= \lim_{\varepsilon \rightarrow 0} \langle \alpha | T(G(\hat{p}(t))F(\hat{\alpha}(t - \varepsilon))) | \alpha_0 \rangle \\
 &= \langle \alpha | G(\hat{p}(t))F(\hat{\alpha}(t)) | \alpha_0 \rangle \quad (27)
 \end{aligned}$$

so if the quantum averages are presented in normal form (all $\hat{p}(t)$ to left of $\hat{\alpha}(t)$), they can be interpreted directly in terms of the above functional integral.

Readers familiar with the path integral formulation of classical statistical mechanics (de Dominicis and Peliti 1978) will observe that there is no Jacobian factor in \mathcal{L} (25). Many authors have discussed this point (Leschke and Schmutz 1977, Langouche *et al* 1979); however, it is instructive to consider the following reformulation. Trivially rewriting the Hamiltonian \hat{H} (10) in the form

$$\begin{aligned}
 \hat{H}' &= (1 - \gamma)(\hat{p}A(\hat{\alpha}) - i(\hat{p})^2 B(\hat{\alpha})) + \gamma(A(\hat{\alpha})\hat{p} - iB(\hat{\alpha})(\hat{p})^2) \\
 &= \gamma([\hat{p}, A(\hat{\alpha})] - i[(\hat{p})^2, B(\hat{\alpha})]) \quad (28)
 \end{aligned}$$

where the commutators satisfy (see (11))

$$\begin{aligned}
 [\hat{p}, A(\hat{\alpha})] &= i \frac{\partial A(\hat{\alpha})}{\partial \hat{\alpha}} \\
 [(\hat{p})^2, B(\hat{\alpha})] &= i \left(\hat{p} \frac{\partial B(\hat{\alpha})}{\partial \hat{\alpha}} + \frac{\partial B(\hat{\alpha})}{\partial \hat{\alpha}} \hat{p} \right)
 \end{aligned}
 \tag{29}$$

one finds that the Lagrangian now admits a ‘Jacobian’

$$\mathcal{L}' = \mathcal{L} + \gamma \left(i \frac{\partial A(\alpha)}{\partial \alpha} + 2p \frac{\partial B(\alpha)}{\partial \alpha} \right)
 \tag{30}$$

whilst the equal time relation (27) is modified in the form

$$\langle G(p(t))F(\alpha(t)) \rangle_{\alpha_0} = \langle \alpha | (G(\hat{p}(t))F(\hat{\alpha}(t)) - \gamma [G(\hat{p}(t)), F(\hat{\alpha}(t))]) | \alpha_0 \rangle.
 \tag{31}$$

Operationally, the choice $\gamma = 0$ corresponding to a normally ordered Hamiltonian is obviously preferable; however, of course, providing one uses the discretisation consistently, no problems arise (see Langouche *et al* 1979).

The generalisation of our multitime expressions (20), (22) and (23) to include spatial (cell-to-cell) diffusion is now straightforward. Choosing the natural representation ($\gamma = 0$) one finds

$$\begin{aligned}
 \langle \langle x_i(t)x_j(t') \rangle \rangle_{\alpha_0} &\stackrel{t > t'}{=} \int [d\alpha] \int [dp] \exp\left(-i \int_{t_0}^{t'} dt \mathcal{L}\right) \left(\alpha_i(t)\alpha_j(t') + i\alpha_i(t)p_j(t')\alpha_j(t') \right) \\
 \langle \langle x_i(t)x_j(t')x_k(t'') \rangle \rangle_{\alpha_0} &\stackrel{t > t' > t''}{=} \int [d\alpha] \int [dp] \exp\left(-i \int_{t_0}^{t'} dt \mathcal{L}\right) \left(\alpha_i(t)\alpha_j(t')\alpha_k(t'') \right. \\
 &\quad \left. + i\alpha_i(t')\alpha_j(t')p_k(t'')\alpha_k(t'') \right) \\
 \langle \langle x_i(t)x_j(t')x_k(t'') \rangle \rangle_{\alpha_0} - \delta_{jk} \langle \langle x_i(t)x_j(t') \rangle \rangle_{\alpha_0} &\stackrel{t > t'}{=} \int [d\alpha] \int [dp] \exp\left(-i \int_{t_0}^{t'} dt \mathcal{L}\right) \left(\alpha_i(t)\alpha_j(t')\alpha_k(t') \right. \\
 &\quad \left. + i\alpha_i(t)(p_j(t') + p_k(t'))\alpha_j(t')\alpha_k(t') - \alpha_i(t)p_j(t')p_k(t')\alpha_j(t')\alpha_k(t') \right)
 \end{aligned}
 \tag{32}$$

where the Lagrangian \mathcal{L} is now given by the relation

$$\mathcal{L} = \sum_{i=1}^N p_i(t) \left(\dot{\alpha}_i(t) - \sum_{j=1}^N D_{ij}\alpha_j(t) + A(\alpha_i(t)) - ip_i(t)B(\alpha_i(t)) \right).
 \tag{33}$$

By analogy with classical statistical mechanics it is useful to introduce source field $h_i(t)$ coupled to $(-p_i(t))$ or $r_i(t)$ coupled to $(p_i(t)\alpha_i(t))$ in terms of which we may rewrite (32) as follows. We have either

$$\begin{aligned}
 \langle \langle x_i(t)x_j(t') \rangle \rangle_{\alpha_0} &\stackrel{t > t'}{=} \left(1 + \frac{\partial}{\partial h_j(t')} \right) \langle \alpha_i(t)\alpha_j(t') \rangle_{\alpha_0, h=r=0} \\
 \langle \langle x_i(t)x_j(t')x_k(t'') \rangle \rangle_{\alpha_0} &\stackrel{t > t' > t''}{=} \left(1 + \frac{\partial}{\partial h_k(t'')} \right) \langle \alpha_i(t)\alpha_j(t')\alpha_k(t'') \rangle_{\alpha_0, h=r=0}
 \end{aligned}
 \tag{34}$$

$$\begin{aligned} \langle\langle x_i(t)x_j(t')x_k(t') \rangle\rangle_{\alpha_0} - \delta_{jk}\langle\langle x_i(t)x_j(t') \rangle\rangle_{\alpha_0} \\ = \stackrel{t > t'}{=} \left(1 + \frac{\partial}{\partial h_j(t')} + \frac{\partial}{\partial h_k(t')} - \frac{\partial^2}{\partial h_j(t') \partial h_k(t')} \right) \langle\alpha_i(t)\alpha_j(t')\alpha_k(t')\rangle_{\alpha_0, h=r=0} \end{aligned}$$

or perhaps more simply

$$\begin{aligned} \langle\langle x_i(t)x_j(t') \rangle\rangle_{\alpha_0} &\stackrel{t > t_0}{=} \langle\alpha_i(t)\alpha_j(t')\rangle_{\alpha_0} - \frac{\partial}{\partial r_j(t')} \langle\alpha_i(t)\rangle_{\alpha_0, h=r=0} \\ \langle\langle x_i(t)x_j(t')x_k(t'') \rangle\rangle_{\alpha_0} &\stackrel{t > t' > t''}{=} \langle\alpha_i(t)\alpha_j(t')\alpha_k(t'')\rangle_{\alpha_0} - \frac{\partial}{\partial r_k(t'')} \langle\alpha_i(t)\alpha_j(t')\rangle_{\alpha_0, h=r=0} \end{aligned} \tag{35}$$

$$\begin{aligned} \langle\langle x_i(t)x_j(t')x_k(t'') \rangle\rangle_{\alpha_0} - \delta_{jk}\langle\langle x_i(t)x_j(t') \rangle\rangle_{\alpha_0} \\ = \stackrel{t > t'}{=} \langle\alpha_i(t)\alpha_j(t')\alpha_k(t'')\rangle_{\alpha_0} - \frac{\partial}{\partial r_j(t')} \langle\alpha_i(t)\alpha_k(t'')\rangle_{\alpha_0, h=r=0} \\ - \frac{\partial}{\partial r_k(t'')} \langle\alpha_i(t)\alpha_j(t')\rangle_{\alpha_0, h=r=0} + \frac{\partial^2}{\partial r_j(t') \partial r_k(t'')} \langle\alpha_i(t)\rangle_{\alpha_0, h=r=0} \end{aligned}$$

where the Poissonian averages are computed with the enhanced Lagrangian $\mathcal{L}' = \mathcal{L} + \sum_{i=1}^N [(p_i(t)\alpha_i(t))r_i(t) - p_i(t)h_i(t)]$. As one would expect in the equal time limit (34) and (35) reduce to known expressions (6) and (7).

Given the Poisson transform in conjunction with the connection formula, one therefore has via this functional integral formulation a very flexible dynamic description. As an example, let us look more closely at the Schlögl model (1). In the continuum limit ($l \rightarrow 0$ at fixed densities $\rho(\mathbf{r}, t) \equiv x_i/l^d$, $\alpha(\mathbf{r}, t) \equiv \alpha_i/l^d$ with $\tilde{\alpha}(\mathbf{r}, t) \equiv p_i$ in d spatial dimensions), the Lagrangian \mathcal{L} (33) takes the simply polynomial form

$$\begin{aligned} \mathcal{L} = \int d\mathbf{r}^d \left\{ \tilde{\alpha}(\mathbf{r}, t) \left[\left(-D\nabla^2 + \frac{\partial}{\partial t} + r \right) \alpha(\mathbf{r}, t) + u\alpha^2(\mathbf{r}, t) \right] \right. \\ \left. - i\tilde{\alpha}^2(\mathbf{r}, t)(v\alpha(\mathbf{r}, t) - u\alpha^2(\mathbf{r}, t)) - \tilde{\alpha}(\mathbf{r}, t)h \right\} \end{aligned} \tag{36}$$

whilst the connection formulae are now

$$\langle\langle \rho(\mathbf{r}, t)\rho(\mathbf{r}', t') \rangle\rangle_{\alpha_0} = \langle\alpha(\mathbf{r}, t)\alpha(\mathbf{r}', t')\rangle_{\alpha_0} - \frac{\partial}{\partial r(\mathbf{r}', t')} \langle\alpha(\mathbf{r}, t)\rangle \tag{37}$$

etc. As one would expect, the couplings D , r , u , v and h are related to the reaction-diffusion model (2) via

$$\begin{aligned} r &= (k_1B - k_2A) & u &= k_4l^d \\ v &= k_2A & h &= k_3Cl^{-d} \end{aligned} \tag{38}$$

and thus are fully determined. For such polynomial field theories a huge variety of powerful techniques are available. These range from the familiar loop expansion through which the mean field (or Gaussian) approximation can be systematically improved to sophisticated uses of the renormalisation group (Brezin *et al* 1975). In particular it is interesting to observe that the mean field behaviour is fully described

by extremals of the functional $\Gamma(M, \hat{M})$ (de Dominicis and Peliti 1978)

$$\Gamma(M, \hat{M}) = \hat{M} \left[\left(-D\nabla^2 + \frac{\partial}{\partial t} + r \right) M + uM^2 \right] - i(\hat{M})^2(vM - uM^2) \quad (39)$$

so that our formalism leads naturally to a ‘generalised thermodynamics’, containing a response field \hat{M} not linked by a fluctuation-dissipation theory to the behaviour of the density $M \equiv \langle \rho \rangle$. Explicitly one solves (Elderfield and Vvedensky 1985)

$$\frac{\partial \Gamma}{\partial M(\mathbf{r}, t)} = 0 = \frac{\partial \Gamma}{\partial \hat{M}(\mathbf{r}, t)} - h \quad (40)$$

for $M = \langle \alpha \rangle$ and $\hat{M} = 0$ (causality), obtaining the Poisson correlation/response functions then via

$$C_\alpha(\mathbf{r}, t, \mathbf{r}', t') = i \int dx^d ds R(\mathbf{r}, t, \mathbf{x}, s) \left(\frac{\partial^2 \Gamma}{\partial \hat{M}(\mathbf{x}, s)^2} \right) R(\mathbf{x}, s, \mathbf{r}', t') \\ \int dx^d \int ds \left(R_\alpha(\mathbf{r}, t, \mathbf{x}, s) \frac{\partial^2 \Gamma}{\partial \hat{M}(\mathbf{x}, s) \partial M(\mathbf{r}', t')} \right) = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (41)$$

where we define

$$R_\alpha(\mathbf{r}, t, \mathbf{r}', t') \equiv \frac{\partial \langle \alpha(\mathbf{r}, t) \rangle}{\partial h(\mathbf{r}', t')} \\ C_\alpha(\mathbf{r}, t, \mathbf{r}', t') \equiv \langle (\alpha(\mathbf{r}, t) - \langle \alpha(\mathbf{r}, t) \rangle) (\alpha(\mathbf{r}', t') - \langle \alpha(\mathbf{r}', t') \rangle) \rangle.$$

Using the connection formulae (37) we then have a complete mean field description.

Several interesting features are already evident in mean field theory. From (39) and (40) we see that the correlation function $C_\alpha(\mathbf{q}, \mathbf{q}', t)$ in the vicinity of a stationary state takes the form

$$C_\alpha(\mathbf{q}, \mathbf{q}', t) = \delta(\mathbf{q} - \mathbf{q}') \left(\exp[-D(q^2 + \xi^2)|t|] \frac{2(vM - uM^2)}{D(q^2 + \xi^2)} \right) \quad (42)$$

and therefore is not intrinsically positive (f is a quasiprobability). Indeed, in equilibrium when the two reactions (1) balance independently (no fluxes of A, B, C) the connected *correlation function vanishes* so the Poisson representation has a fundamental significance for these systems. Using the connection formulae one predicts for the chemical fluctuations a correlation function of the form

$$C_\rho(\mathbf{q}, \mathbf{q}', t) = \delta(\mathbf{q} - \mathbf{q}') \left[\exp[+D(q^2 + \xi^2)|t|] \left(\frac{2(vM - uM^2)}{D(q^2 + \xi^2)} + M \right) \right] \quad (43)$$

which is to be contrasted with those expected on the basis of naive Landau-Ginzburg approaches

$$C_\rho(\mathbf{q}, \mathbf{q}', t) = \delta(\mathbf{q} - \mathbf{q}') \left(\frac{A}{D(q^2 + \xi^2)} \right) \exp[-D(q^2 + \xi^2)|t|]. \quad (44)$$

Here A is some *positive* constant. At equal time *and* large distances (43) reduces to the recent result of Nicolis and Malek Mansour (1984). Confirmation of (43) via real (or computer) experiments should be possible, for simple systems.

3. Conclusions

To conclude, we have demonstrated how the Poisson transform ($\mathcal{G}\mathcal{C}$) in conjunction with the connection formulae developed here can provide a comprehensive description for these intrinsically non-equilibrium (open) systems. For the Schlögl model (1) we have indicated how our formalism reproduces and generalises recent mean field computations (Nicolis and Malek Mansour 1984). We are currently studying the Schlögl model and Brusselator in greater depth, since for the first time we are in an ideal position to study the intrinsically non-equilibrium properties of these systems. In particular we are using the generalised 'thermodynamic' potential $\Gamma(M, \hat{M})$ (29) to elucidate the local/global stability criteria.

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