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Irreversibility Paradox Revised: Onset of a Center Manifold in Dissipative Systems

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A center-manifold-reduced Fokker–Planck equation is derived, starting from a time-reversible Liouville equation. The derivation is valid when there is a large separation of relaxation-time scales causing the phase-space contraction near a dynamic critical point. The paradox of breaking of time-reversal symmetry in the resulting Fokker–Planck equation at the onset of the center manifold is clarified.

1. INTRODUCTORY REMARKS AND MOTIVATIONS

We shall consider nonequilibrium systems whose macrostates are characterized by a set of thermal averages of certain order parameters and the products of these order parameters. Specifically, we shall concentrate upon the case in which there exists a statistical subordination of the fast-relaxing macroscopic degrees of freedom of the system to the excited subordinated modes near a dynamic critical point (Fernández, 1986; Fernández and Rabitz, 1987). This phase-space contraction can be accounted for by means of the stochastic center manifold theory (Marsden, 1973; Fernández and Sinanoğlu, 1984; Fernández and Rabitz, 1987). For a sufficiently large separation of relaxation time scales, the system is confined to a locally attractive, locally invariant surface determined by the functional dependence of the fast-relaxing modes to the order parameters. The order parameters thus become the center manifold (CM) coordinates of the system. This treatment has already been implemented to determine the strength of far-from-equilibrium fluctuations at the onset of a dissipative structure in chemical kinetics (Fernández and Sinanoğlu, 1984). Furthermore, it has become useful in the realm of Rayleigh–Bénard convection, in

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particular, to elucidate the role of random sources in the transition to a convective roll pattern (Fernández and Rabitz, 1987). The analysis reveals that any extrapolation from near-equilibrium situations making use of a Langevin source is of no avail, the fluctuations being at least three orders of magnitude larger than their equilibrium counterparts (Fernández and Rabitz, 1987).

The problem we shall deal with can be best posed as follows: *How can a nonequilibrium Fokker–Planck (FP) equation for the order parameters be derived from the time-reversible Liouville equation for the microstate probability distribution function?*

We shall show that the paradox of the emergence of irreversibility at the onset of the CM can be explained since *the breakdown of the time-reversal symmetry is introduced in the boundary condition: The causal character of the solution is given by the coincidence of the microstate probability distribution function with a CM microstate distribution in the remote past.* The CM microstate distribution is determined by the probability distribution for the order parameters and it does not depend explicitly on the coordinates and momenta of the individual particles, but only on the order parameters.

2. BASIC TENETS OF CM THEORY AND THE CONSTRUCTION OF THE CM MICROSTATE DISTRIBUTION

In order to fix notation, let us denote by X the vector of macrovariables. Upon a nonsingular transformation, we shall assume the system is already in Poincaré–Jordan normal form, that is, the Jacobian matrix of the system at the nonequilibrium state is in Jordan normal form (Marsden, 1973; Fernández and Sinanoğlu, 1984; Fernández and Rabitz, 1987). In other words, the fast-relaxing degrees of freedom have been separated from the enslaved coordinates and the following decomposition holds:

$$X = X_s + X_f \tag{1}$$

where X_s denotes generically the vector of CM coordinates and X_f denotes the vector of fast-relaxing degrees of freedom. One of the basic tenets of the CM theory is that after a transient equal to the supreme of the relaxation times for the fast modes, the following relation holds:

$$\langle X_{fj} \rangle = F_j(\langle X \rangle, \{\langle X_i X_k \rangle\}, \{\langle X_i X_k X_n \rangle\}, \ldots) \tag{2}$$

where $X_i (i = 1, 2, \ldots, s)$ is a component of the vector X_s, F_j is the CM function determining the functional dependence that characterizes the statistical enslavement of the fast-relaxing degrees of freedom X_{fj} (Fernández and Rabitz, 1987), and the angular brackets denote a thermal or statistical average. The second basic tenet of the CM theory is that the probability density functional $P = P(X, t)$ can be factorized as follows:

$$P = Q_s \times Q_f \tag{3}$$

$$Q_s = Q_s(X_s, t) \tag{4}$$

$$\begin{aligned} Q_f &= Q_f(X_f \mid X_s) \\ &= \prod_{j\geq 1} (g_j/\pi)^{1/2} \exp[-g_j(X_{fj} - \langle X_{fj} \rangle)^2] \end{aligned} \tag{5}$$

The last equation admits a rigorous derivation and it reveals that the fast-relaxing degrees of freedom are distributed along a strip of width $w = (2g_j)^{1/2}$ along the CM. Thus, the time-dependent factor represents the statistical subordination and it is given in the form of a conditional probability Gaussian peaked at the CM.

The smeared FP equation for Q_s can be obtained upon integration of the general FP equation satisfied by P along the CM, that is, by integration with respect to the fast-relaxing variables, making use of equation (5). We now introduce a microstate distribution induced by Q_s. This distribution will be called the CM microstate distribution and will be denoted $\beta = \beta(t)$. This functional is not explicitly dependent on the position and momenta of the individual particles; it depends on them through X_s. It has the general form

$$\beta(t) = \exp[-N(t) - B(X_s', t)] \tag{6}$$

where $N(t)$ is found from the normalization condition and $B(X_s', t)$ is determined by imposing the condition that the thermal average with respect to β of $\delta(X_s' - X_s)$ should be the same as the true average with respect to the microstate distribution function $p(t)$:

$$\langle \delta(X_s' - X_s) \rangle_\beta = \langle \delta(X_s' - X_s) \rangle \tag{7}$$

In this equation it is understood that X_s' corresponds to the order parameter vector, dependent on the positions q_m and on the momenta p_m of the individual particles; and that X_s is a specific value of the vector X_s'. In what follows, $I(\cdot)$ shall denote integration over the coordinates and momenta of all the particles with the normal factor $1/(h^{3N} \cdot N!)$. Thus, from equation (7), we can derive the equation for β:

$$\beta(t) = \int [I(\delta(X_s' - X_s))]^{-1} Q(X_s, t)\, \delta(X_s' - X_s)\, dX_s \tag{8}$$

This last result follows from the obvious relation

$$\langle \delta(X_s' - X_s) \rangle = Q_s(X_s, t) \tag{9}$$

3. DERIVATION OF THE SMEARED FP EQUATION FOR Q_s STARTING FROM THE LIOUVILLE TIME-REVERSIBLE EQUATION

We shall show that the source of irreversibility in the procedure of derivation of a smeared FP equation for the order parameters does not come from the Liouville equation, but from the causal character of the boundary conditions imposed. The starting point is the Liouville equation for $p(t)$:

$$\frac{\partial}{\partial t} p(t) + iLp(t) = 0 \tag{10}$$

where L is the Liouville operator: $iLp = \{H, p\}$, with H the Hamiltonian of the system.

The source of irreversibility is introduced by assuming that, in agreement with the CM reduction, the solution of equation (10) coincides with the CM microstate distribution at the instant t_0 in the remote past:

$$p(t) = \exp[-iL(t - t_0)]\, \beta(t_0) \tag{11}$$

In order to get rid of this unphysical dependence on the initial moment t_0, we introduce a smoothing procedure by averaging over all initial moments t_0' between t_0 and t:

$$p(t) = T^{-1} \int_{t_0}^{t} \exp[-iL(t - t_0')]\, \beta(t_0')\, dt_0', \qquad T = t - t_0 \tag{12}$$

that is, over the length of time T which is very near the thermodynamic limit $T \to \infty$ (Bogolyubov, 1978).

But this procedure leads to a breakdown of the time-reversal symmetry, since the function given by equation (12) is a solution not of the Liouville equation in its original form, but of a new equation containing an infinitesimal source describing the relaxation of $p(t)$ to the CM:

$$\frac{\partial}{\partial t} p + iLp = -T^{-1}[p(t) - \beta(t)] \tag{13}$$

This relaxation to the CM has an extremely slow mean time if we operate near the thermodynamic limit. Therefore, the source of irreversibility due to "contamination" with the phenomenological CM contraction can be made arbitrarily small.

In the spirit of Mori's projection operator formalism (Kawasaki, 1970; Mori, 1965), we shall define a projector in order to restrict the system to the CM, that is, we transform a microstate distribution A into an order parameter distribution UA:

$$UA = \int [I(\delta(X_s' - X_s))]^{-1} I(A\delta(X_s' - X_s))\, \delta(X_s' - X_s)\, dX_s \tag{14}$$

$$UA = UA(X_s', t) \tag{15}$$

It can be readily verified that this operator is a projection operator and that it has the additional properties

$$Up = \beta \tag{16}$$

$$U\beta = \beta \tag{17}$$

Therefore, we can write an equation for β in the compact form

$$\frac{\partial}{\partial t}\beta = U\dot{p} = -UiL(p - \beta) - UiL\beta \tag{18}$$

Making use of this formalism, we can now derive the generalized force $M(X_s)$ responsible for the diffusive pressure produced by the far-from equilibrium fluctuations. This diffusive pressure competes with the deterministic fast drift toward the CM determined by the separation of relaxation time scales. Therefore, the generalized forces determine the Gaussian width of the probability density Q_f about the CM. In other words, these forces are orthogonal to the CM:

$$M(X_s) = (1 - U)\, \delta(X_s' - X_s)\, iLX_s' \tag{19}$$

The conjugated fluxes, orthogonal to the CM, are

$$J(X_s) = -\frac{\partial}{\partial X_s} M(X_s) = (1 - U) iL\, \delta(X_s' - X_s) \tag{20}$$

The thermal average of the fluxes is therefore given by

$$\langle J(X_s)\rangle = \frac{\partial}{\partial X_s} \int dX_s' \int_{-\infty}^{t} dt' \times \exp[T^{-1}(t' - t)]\, K(X_s', X_s, t - t')\, V(X_s', t') \tag{21}$$

where the kernel K is given by

$$K(X_s', X_s, t) = I(M(X_s) \exp[(1 - U) itL]\, M(X_s')) \tag{22}$$

and

$$V(X_s', t) = \frac{\partial}{\partial X_s'} \left(\frac{Q_s(X_s', t')}{L(X_s')} \right) \tag{23}$$

where

$$L(X_s) = I(\delta(X'_s - X_s)) \tag{24}$$

Finally, the speed of the order parameters is given by

$$W(X_s) = I(\delta(X'_s - X_s) iLX'_s)/L(X_s) \tag{25}$$

Thus, we arrive at the retarded FP equation for Q_s:

$$\frac{\partial}{\partial X_s} Q_s(X_s, t) = -\frac{\partial}{\partial X_s} W(X_s) Q_s(X_s, t) + \langle J(X_s) \rangle \tag{26}$$

The explicit form of the thermally averaged flux orthogonal to the CM is given explicitly in equation (21). This equation is exact and it is derived from first principles, the projection operator U being formally the same as the Zwanzig operator (Kawasaki, 1970; Mori, 1965) (the set of macrovariables is reduced to the CM coordinates).

Not surprisingly, the smeared FP equation (26) reveals a breakdown of the time-reversal symmetry. There is no contradiction in this fact, since the boundary conditions reflected in equation (11) for the solution of the Liouville equation were introduced *a priori*, taking into account the attractive nature of the CM. This is the source of irreversibility, since the onset of a center manifold is in itself irreversible. The relevance of this work for the analysis of dissipative structures in chemical kinetics far from equilibrium is clear once we recognize that a dissipative structure can be associated with a CM in a natural way (Marsden, 1973; Fernández, 1986; Fernández and Sinanoğlu, 1984; Fernández and Rabitz, 1987).

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