

Self-Organization in Complex Media

G. Nicolis* and V. Altares

Faculté des Sciences, Université Libre de Bruxelles, Campus Plaine, CP 231, 1050 Bruxelles, Belgium
(Received: October 20, 1988)

Reaction-diffusion dynamics in complex media is analyzed. The diffusion operator is decomposed into a deterministic and a random part. In the absence of chemical reactions it is shown that randomness enhances the rate of spread of an initial inhomogeneity and reduces the stationary diffusion flux. When chemical reactions are included, an augmented reaction-diffusion equation is derived, featuring an effective diffusion coefficient that depends explicitly on the chemical kinetics. The influence of randomness in the onset of chemical instabilities leading to self-organization is discussed.

1. Introduction

Dick Noyes' classic study of the oscillatory behavior of the Belousov-Zhabotinski reagent has been instrumental in the development of a new and active field of chemical science devoted to self-organization and nonlinear phenomena. It is a privilege and a pleasure to dedicate to him the present short communication as a tribute to his brilliant contributions.

The typical framework within which self-organization phenomena in chemistry have been studied is that of reaction-diffusion systems¹

$$\partial X_i / \partial t = F_i(X_i, \lambda) + D_i \nabla^2 X_i \quad (1)$$

Here X_i and D_i denote respectively the concentration and diffusion coefficients of species i , F_i the rate laws (generally nonlinear functions of X_i 's), and λ the control parameters. It is usually assumed that the medium is isothermal and ideal (no cross effects and no concentration dependencies in D_i), although some attempts to relax this latter condition have been reported.² More to the point for the purposes of our present discussion, it is also assumed that the medium is homogeneous and isotropic or, equivalently, that the diffusion coefficients D_i and the rate functions F_i have no explicit space dependence.

Although the above assumptions are frequently fulfilled under laboratory conditions, there is little doubt that they will in general fail in real-world materials. A rough catalytic surface, a rock, a piece of metal under load, contain inevitably some degree of disorder, notably in the form of imperfections and defects. A biological material, say a membrane on which Ca^{2+} ions are diffusing, is far from being a perfect lattice. Even in the laboratory scale experiments aiming to detect space patterns are currently being developed,^{3,4} in which porous or dispersed materials play a prominent role.

A chemical dynamics taking place in a medium of the above kind will be affected by the spatial disorder in two respects: an explicit space dependence of the distribution of the major chemicals feeding the reactor and an explicit dependence on the spatial location of the rate at which diffusion will take place. Our principal objective in the present work is to study the new effects arising from these phenomena in the limiting case in which space dependencies are modeled as a random process.

In section 2 we describe the model adopted and discuss the physical origin of the assumptions involved. In section 3 we study the behavior in the absence of reactions, whose effect is considered in section 4. We end with a short discussion on the role of random diffusion in the onset of a chemical instability.

2. The Model

Let X be a passive scalar (concentration field) transported in an heterogeneous medium. Its instantaneous profile is given by

the solution of the mass conservation law

$$\partial X / \partial t = -\nabla \cdot \mathbf{J} \quad (2)$$

supplemented with the phenomenological relation

$$\mathbf{J} = -L \nabla \frac{\mu_X(X, T, r)}{T} \quad (3)$$

where L is the Onsager coefficient and μ_X the chemical potential of X :

$$\mu_X = \mu_0 + RT \ln a$$

a being the activity. In an isothermal system (3) becomes

$$\mathbf{J} = -\frac{LR}{a} \nabla a$$

Introducing the diffusion and activity coefficients D and γ respectively through

$$D = LR/X \quad (4a)$$

$$a = \gamma X \quad (4b)$$

we can finally write (2) in the form

$$\frac{\partial X}{\partial t} = \nabla \cdot D(r) \frac{1}{\gamma(r, a)} \nabla \gamma(r, a) X \quad (5)$$

We have introduced an explicit space dependence of D and γ in order to account for the complexity of the medium. In what follows we shall assume that the space dependence of the activity coefficient is weaker than the dependence of $D(r)$, in which case γ can be eliminated from the right-hand side.

Furthermore, we shall model the complexity of the medium by introducing a *fluctuating part* in the diffusion coefficient, which will be assimilated to a random process with continuous realizations. The scalar field X will then also become a random process obeying

$$\partial X / \partial t = \nabla \cdot D(r) \nabla X \quad (6a)$$

with

$$D = D_0 + D_1(r), \quad \langle D_1(r) \rangle = 0 \quad (6b)$$

where the brackets denote ensemble average, i.e., an average over the different realizations of the stochastic process $D_1(r)$.

Disordered media are usually modeled by random walks on regular lattices with random transition probabilities.^{5,6} In this case, the scaling law of the mean-square displacement depends ultimately on the type of probability distribution chosen for the transition probabilities.⁶ Classical diffusion is expected when the average of the inverse of the transition probability exists; otherwise anomalous diffusion may appear.

We make now a possible connection between our continuous formalism and a discretized lattice version. In the latter approach,

(1) Nicolis, G.; Prigogine, I. *Self Organization in Non-Equilibrium Systems*; Wiley: New York, 1977.

(2) Li, R. S.; Nicolis, G. *J. Chem. Phys.* **1981**, *77*, 2365. Li, R. S.; Nicolis, G.; Frisch, H. L. *J. Phys. Chem.* **1981**, *85*, 1907.

(3) Noszticzius, Z.; Horsthemke, W.; McCormick, W. D.; Swinney, M. L.; Tam, W. Y. *Nature* **1987**, *329*, 619.

(4) Maseko, J.; Showalter, K. Private communication.

(5) Havlin, S.; Ben-Avraham, D. *Adv. Phys.* **1987**, *36*, 695.

(6) Alexander, S.; Bernasconi, J.; Schneider, W. R.; Orbach, R. *Rev. Mod. Phys.* **1981**, *53*, 175.

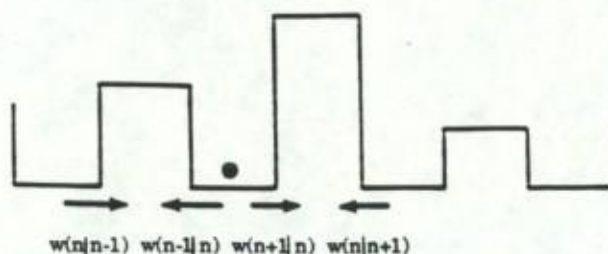


Figure 1. Schematic representation of diffusion in a complex medium viewed as the motion across a random distribution of potential barriers.

the probability $P_n(t)$ of a random walker to be at site n at time t obeys a stochastic master equation:

$$dP_n(t)/dt = w(n|n+1)P_{n+1}(t) + w(n|n-1)P_{n-1}(t) - (w(n-1|n) + w(n+1|n))P_n(t) \quad (7)$$

where $w(n|n+1)$ is the transition probability per unit time of a random walker to jump from site $n+1$ to site n and is itself a random function of site n . If these transition probabilities are related to the probability of hopping across a barrier between two adjacent sites, we have (cf. Figure 1)

$$w_n = w(n|n+1) = w(n+1|n) \quad (8)$$

Equation 7 is then rewritten in the form

$$dP_n(t)/dt = w_n(P_{n+1}(t) - P_n(t)) + w_{n-1}(P_{n-1}(t) - P_n(t)) \quad (9)$$

Since the total mass of the transported quantity is conserved, the concentration $X(r,t)$ is proportional to the probability of a random walker in a particular realization of $D(r)$ to be at a position r at time t . Equation 9 is therefore a discretized version of (6). The diffusion coefficient $D(r)$ in (1) is the limit $D(r) = \lim_{l \rightarrow 0} w(r)/l^2$, where l denotes the mesh size of the lattice.⁷ The statistical properties of $D(r)$ are then related to those of the transition probabilities of a particular lattice.

The above arguments can easily be extended to an isotropic system undergoing chemical reactions, since for such a system there is no phenomenological coupling between reaction rate and diffusion flux. We thus obtain for such a medium the generalized reaction-diffusion equation

$$\partial X/\partial t = F(X,\lambda) + \nabla \cdot D(r) \nabla X \quad (10)$$

being understood that the diffusion coefficient D comprises again a "deterministic" and a "random" part as in (6b).

3. Properties of the Stochastic Diffusion Operator

In this section we explore some properties of the solutions of (10) in the absence of chemical reactions. We first study the time-dependent behavior of the first nontrivial moment of the concentration field.

Normalizing the total mass to unity, multiplying both sides of (6a) by the square of the displacement r , integrating over space, and assuming that X and $\partial X/\partial r$ tend to zero sufficiently rapidly for $r \rightarrow \pm\infty$, we obtain in a one-dimensional infinite medium

$$\begin{aligned} \frac{d}{dt} \langle r^2 \rangle &= \int_{-\infty}^{\infty} dr r^2 \frac{\partial}{\partial t} (X(r,t)) \\ &= -2 \int_{-\infty}^{\infty} dr r \left\langle D(r) \frac{\partial X(r,t)}{\partial r} \right\rangle \end{aligned} \quad (11)$$

The contribution to (11) arising from the deterministic part D_0 of D is straightforward. Upon performing a second partial integration, it yields

$$d \langle r^2 \rangle_{\text{det}}/dt = 2D_0 \quad (12)$$

To evaluate the contribution of the random part to the right-hand side, we need to specify further the statistical properties of $D_1(r)$. We will assume that $D_1(r)$ defines a homogeneous Gaussian

random process whose correlation function

$$g(r) = \langle D_1(0) D_1(r) \rangle \quad (13a)$$

behaves in the origin $r = 0$ in an exponential fashion. This implies, in particular, that the second derivative at the origin $g''(0)$, is positive, which allows us to introduce a correlation length l through

$$l^{-2} = g''(0)/g(0) \quad (13b)$$

The evaluation of the random part of (11) will make use of the Novikov theorem⁸ stating that if $\mathcal{F}[d]$ is a functional of a Gaussian random field $d(r)$, then

$$\langle d(r) \mathcal{F}[d] \rangle = \int dr' g(r-r') \left\langle \frac{\delta \mathcal{F}[d]}{\delta d(r')} \right\rangle$$

where $\delta/\delta d$ denotes functional differentiation. In our case (cf. (11)) the field $d(r)$ is the random part $D_1(r)$ of D , while the functional \mathcal{F} is the space derivative of X , itself a functional of $D_1(r)$ through (6). The details of the calculation are given in the Appendix, the final result being

$$\frac{d}{dt} \langle r^2 \rangle = 2 \frac{g(0)}{l^2} t \quad (14)$$

Combining (13) and (14) and integrating over time, we finally obtain

$$\langle r^2 \rangle = 2D_0 t + (g(0)/l^2) t^2 \quad (15)$$

This result shows the appearance of anomalous diffusion induced by the fluctuations of the diffusion coefficient and tending to enhance the spreading of an initial inhomogeneity in comparison to the classical case. This is to be contrasted to what is found in fractal lattices or percolation clusters where a scaling law of the form⁵

$$\langle r^2 \rangle \sim t^{2/d} \quad d > 2$$

is obtained, indicating the slowing down of diffusion.

It is interesting to remark that numerical simulations in a three-dimensional random field system (cubic lattice) and Langevin equation analysis lead to a mean-square displacement⁹ which is asymptotically proportional to t^2 . Moreover, for short times an interplay between classical and anomalous diffusion was observed. Our result seems therefore in good agreement with these studies.

On the other hand, in his study of random walk in a one-dimensional lattice with random transition probabilities $p_n, q_n = 1 - p_n, p_n = 1/2 + \epsilon \xi_n$, with ξ_n taking at random the values ± 1 or -1 , Sinai has found a subdiffusive behavior corresponding to a logarithmic scaling law.¹⁰ We believe that the difference with our results arises from the assumptions adopted on the statistical properties of $D(r)$, and most particularly from the existence, in our model, of a spatial correlation function displaying a finite characteristic length.

In a different context, anomalous diffusion has been predicted in a heterogeneous porous medium¹¹ when the correlation length of the fluctuating permeability diverges. For a particular class of spectra of the fluctuations, anomalous diffusion also occurs in stratified porous media.^{11,12} These observations stress the fact that, as in random lattices, the type of scaling law is very sensitive to statistical properties of the fluctuating fields.

Let us now turn to the stationary-state solution of (6), expected to arise in a finite system subjected to suitable boundary conditions. In all generality, the mean stationary flux $\langle J \rangle$ will be (cf. (2) and (6))

(8) Novikov, E. *Sov. Phys. JETP* **1965**, *20*, 1290.

(9) Pandey, R. B. *J. Phys.* **1986**, *A19*, 3925. Heinrichs, J.; Kumar, N. *J. Phys.* **1984**, *C17*, 769.

(10) Sinai, Ya. *Theory Probab. Its Appl. (Engl. Transl.)* **1982**, *27*, 256.

(11) Koch, D.; Brady, J. *Phys. Fluids* **1988**, *31*, 965.

(12) Gelhar, L.; Gutjahr, A.; Naff, R. *Water Resour. Res.* **1979**, *15*, 1387. Matheron, G.; De Marsily, G. *Water Resour. Res.* **1980**, *16*, 901.

(7) Gardiner, C. W. *Handbook of Stochastic Methods*; Springer: Berlin, 1983; Chapter 8.

$$\langle \mathbf{J} \rangle = -\langle D(\mathbf{r}) \nabla X \rangle \quad (16a)$$

The point that we would like to explore here is whether this relation can be cast in the form¹³

$$\langle \mathbf{J} \rangle = -\mathcal{D} \nabla \langle X \rangle \quad (16b)$$

where \mathcal{D} is an effective diffusion coefficient. We would also like to relate \mathcal{D} to the deterministic part D_0 and to the statistical properties of $D_1(\mathbf{r})$.

Contrary to the first part of this section in which no smallness parameter had to be introduced, we shall now appeal to perturbation theory. Specifically, we shall assume that the characteristic correlation length l is much less than the characteristic length scale L of variation of the mean concentration field

$$\epsilon = l/L \ll 1 \quad (17)$$

Furthermore, we shall introduce a new length macroscale R and expand the various fields present in powers of ϵ (ref 14)

$$\nabla_r \rightarrow \nabla_r + \epsilon \nabla_R \quad (18a)$$

$$D_1 = \epsilon d_1(\mathbf{r}) \quad (18b)$$

$$X = \langle X(\mathbf{R}) \rangle + x(\mathbf{r}, \mathbf{R}) \quad (18c)$$

$$x = \epsilon x_1 + \epsilon^2 x_2 + \dots \quad (18d)$$

We insert these expansions into (16a) and note that $\langle x \rangle = 0$. We obtain in this way an expression for the mean flux:

$$\langle \mathbf{J} \rangle = -\epsilon D_0 \nabla_R \langle X \rangle - \epsilon \langle d_1(\mathbf{r}) \nabla_r x \rangle \quad (19)$$

To compute the mean value $\langle d_1 \nabla_r x \rangle$ in the right-hand side we need to evaluate x . Expanding (6a) in powers of ϵ , we have in the stationary state the first-order equation

$$D_0 \nabla_r^2 x_1 = 0 \quad (20a)$$

Using the subsidiary condition $\langle x_1 \rangle = 0$ and (20a) yields $x_1 = 0$. To the second order in ϵ (6a) then becomes

$$D_0 \nabla_r^2 x_2 + \nabla_r d_1 \nabla_r \langle X \rangle + D_0 \nabla_R^2 \langle X \rangle = 0 \quad (20b)$$

The subsidiary condition $\langle x_2 \rangle = 0$ requires

$$D_0 \nabla_R^2 \langle X \rangle = 0$$

Equation 20b can now be solved by Fourier transform methods, and we obtain in a three-dimensional system

$$\langle d_1 \nabla_r x_2 \rangle = -\frac{1}{3} \frac{\tilde{g}(0)}{D_0} \nabla_R \langle X \rangle \quad (21)$$

with notation $g(0) = \epsilon^2 \tilde{g}(0)$. Comparing with (16a) and (16b), we are led to identify the effective diffusion coefficient

$$\mathcal{D} = D_0 - \frac{\epsilon^2 \tilde{g}(0)}{3 D_0} \quad (22)$$

This relation shows that fluctuations in the diffusion coefficient decrease the stationary flux of diffusion.¹³ Fluctuations act therefore in an opposite way to fluctuations of a convection field, which enhance diffusion.^{15,16}

4. Reaction-Diffusion Dynamics in a Complex Medium

In this section we report on a first approach aiming to include the effect of chemical reactions (or more generally of source or sink terms) in the stochastic diffusion. For technical simplicity much of our discussion will be limited to the search of stationary-state solutions of (10) in a one-dimensional infinite system involving a single variable. Equation 10 takes then the form

$$F(X) + \frac{d}{dr} D(r) \frac{dX}{dr} = 0 \quad (23)$$

Introducing the decomposition of X into an average and a fluctuating part ((18c)) one obtains from (23) the equations¹⁶

$$\langle F(X) \rangle + \frac{d}{dr} \left(D(r) \frac{d\langle X \rangle}{dr} \right) = 0 \quad (24a)$$

$$F'x + \frac{1}{2} F''(x^2 - \langle x^2 \rangle) + D_0 \frac{d^2 x}{dr^2} + \frac{d}{dr} D_1 \frac{d\langle X \rangle}{dr} + \frac{d}{dr} D_1 \frac{dx}{dr} - \frac{d}{dr} \left(D_1 \frac{dx}{dr} \right) + O(x^3) = 0 \quad (24b)$$

where

$$F' = \frac{dF}{dX} \Big|_{X=\langle X \rangle}$$

It will be assumed that $F' > 0$, in order to ensure that the stationary solution is stable.

To obtain a closed equation for the mean concentration $\langle X \rangle$ from (24a), we insert the multiple scale expansion (18a-d) into (24a). We have to lowest order

$$F(\langle X \rangle) + \frac{1}{2} F'' \langle x^2 \rangle + D_0 \epsilon^2 \frac{d^2 \langle X \rangle}{dR^2} + \epsilon^2 \frac{d}{dR} \langle d_1 \partial_r x \rangle = 0 \quad (25)$$

The terms $\langle x^2 \rangle$ and $\langle d_1 \partial_r x \rangle$ are evaluated from (24b) in an analogous manner as in the preceding section. The first nontrivial contribution obeys

$$F'x_2 + D_0 \frac{\partial^2 x_2}{\partial r^2} + \frac{\partial}{\partial r} d_1(r) \frac{d\langle X \rangle}{dR} = 0 \quad (26)$$

This equation can be solved by Fourier transform methods. The result is

$$x_2(r) = \frac{1}{2\pi} \int dr' \int dk e^{ik(r-r')} \frac{ik}{|F| + D_0 k^2} d_1(r') \frac{d\langle X \rangle}{dR} \quad (27)$$

For the sake of concreteness, we consider the case where the spatial correlation function of the field $d_1(r)$ is exponential

$$g(r) = g(0)e^{-r/l} \quad (28)$$

We obtain finally for small l

$$\left\langle d_1(r) \frac{\partial x_2}{\partial r} \right\rangle = -\frac{\tilde{g}(0)}{D_0} \left[1 - l \left(\frac{|F|}{D_0} \right)^{1/2} \right] \frac{d\langle X \rangle}{dR} \quad (29)$$

and

$$\langle x_2^2 \rangle = \frac{1}{2} \frac{\tilde{g}(0)}{D_0^2} \frac{1}{\left(\left(\frac{|F|}{D_0} \right)^{1/2} + \frac{1}{l} \right)^2} \frac{1}{l} \left[\frac{d\langle X \rangle}{dR} \right]^2 \quad (30)$$

Substituting these expressions into (25) yields the desired closed equation involving solely the mean value X

$$F(\langle X \rangle) + \frac{\epsilon^2}{4D_0^2} F''(\langle X \rangle) g(0) \frac{1}{\left(\left(\frac{|F|}{D_0} \right)^{1/2} + \frac{1}{l} \right)^2} \frac{1}{l} \left[\frac{d\langle X \rangle}{dR} \right]^2 + \epsilon^2 \left(D_0 - \frac{g(0)}{D_0} \left(1 - l \left(\frac{|F|}{D_0} \right)^{1/2} \right) \right) \frac{d^2 \langle X \rangle}{dR^2} \quad (31)$$

We see that the fluctuations give rise to an effective diffusion coefficient

$$\mathcal{D} = D_0 - \epsilon^2 \frac{\tilde{g}(0)}{D_0} \left(1 - l \left(\frac{|F|}{D_0} \right)^{1/2} \right) \quad (32)$$

which now depends explicitly on chemical kinetics. The effective diffusion coefficient is now larger than the effective diffusion in the absence of reactions; in other words, chemical reactions increase the mean diffusion flux. A second type of correction due to the fluctuations in the diffusion coefficient is the presence in

(13) Batchelor, G. K. *Annu. Rev. Fluid Mech.* 1974, 6, 227.

(14) McLaughlin, D. W.; Papanicolaou, G. C.; Pironneau, O. R. *SIAM J. Appl. Math.* 1985, 45, 780.

(15) Koch, D.; Brady, J. J. *Fluid Mech.* 1985, 154, 399.

(16) Puhl, A.; Altares, V.; Nicolis, G. *Phys. Rev.* 1988, A37, 3039.

(17) Feynman, R.; Hibbs, A. *Quantum Mechanics and Path Integrals*; McGraw-Hill: New York, 1965.

the balance equation of a term proportional to the square of the gradient of the mean concentration.

We are now in the position to specify more sharply the role of random diffusion in the onset of instabilities and self-organization. We first derive the time-dependent version of (23) or (29). Let X_0 be a spatially uniform stationary solution used as "reference" state. Suppose, furthermore, that the system operates in a parameter range for which this state is about to lose its stability and give rise to new branches of solutions. Setting

$$\langle X \rangle = X_0 + u$$

one can write to the first order

$$\begin{aligned} F(\langle X \rangle) &= F(X_0) + F'(X_0)u \\ &= F'(X_0)u = -\lambda u \end{aligned}$$

wherein $F'(X_0) = -\lambda$ plays the role of bifurcation parameter. We express the slowing down of the dynamics expected to arise for values of λ near zero by introducing the slow time scale τ :

$$\frac{\partial}{\partial t} = \epsilon^2 \frac{\partial}{\partial \tau}$$

with

$$\lambda = \epsilon^2 \tilde{\lambda} \quad (33)$$

The linearized, time-dependent version of (31) around the reference state X_0 becomes

$$\frac{\partial u}{\partial \tau} = -\tilde{\lambda}u + \mathcal{D} \frac{\partial^2 u}{\partial R^2} \quad (34)$$

This equation entails that one may expect bifurcation of new branches of solutions at exactly the same transition point, $\lambda_c = 0$, independent of the value of \mathcal{D} . On the other hand, the properties of the bifurcating branches and the time-dependent behavior of the system will be strongly affected. For instance, it is well-known that the stability of a solution in a region of hysteretic behavior is favored by an enhancement of \mathcal{D} or, on the contrary, compromised by a reduction of \mathcal{D} .

One kind of transition likely to be affected more drastically by fluctuating diffusion are symmetry-breaking instabilities. These phenomena involve at least two coupled variables and, in an infinite system or a system subjected to periodic or zero flux boundary conditions, require that the diffusion coefficients of the two species be unequal. Now, since the effective diffusion coefficient depends on the kinetics (cf. (32)), we may expect that two species having identical diffusivities in a uniform medium may well be governed by different effective diffusivities in a random medium. This possibility of *fluctuation-induced symmetry breaking* will be taken up in a forthcoming publication.

Finally, it is clear from (26) that in the presence of randomness there will be a dispersion of the concentration field around the average profile given by (31), which will increase with the correlation length l and the mean gradient $d\langle X \rangle/dR$. Self-organization in a random medium will therefore be characterized by patterns displaying an overall order and a superimposed local disorder.

5. Concluding Remarks

In many instances a physicochemical system evolves in a complex medium whose properties are distributed in space in a non-uniform fashion. We have explored some consequences of this complexity on reaction-diffusion dynamics leading to self-or-

ganization, by modeling the diffusion coefficient within the medium as a random process. We have shown that in the absence of chemical reactions diffusion is affected in two quite different ways. In an infinite medium the spreading of an initial inhomogeneity is enhanced, and in a finite medium subjected to boundary conditions the mean stationary diffusion flux is reduced, in the limit in which the correlation length of inhomogeneities of the medium is much less than the system size. When chemical reactions are included, the diffusion flux becomes explicitly dependent on the kinetics. Bifurcations to new branches of solutions may or may not be affected, depending on the number of variables and the type of instability involved.

We believe that the results reported in the present work should be useful in the study of self-organization and nonlinear dynamics in real-world materials. In our view an especially promising field is geology,¹⁸ where one deals with materials with highly variable properties.

Finally, in parallel to the study initiated in this paper it would be useful to pursue work in which the nonuniformity of the medium can be accounted for by a systematic external gradient.¹ This may be a particularly adequate way to model the recent experiments of Noszticzius et al.³ An interesting attempt in this direction is reported in ref 19.

Acknowledgment. We are indebted to Prof. H. Frisch and P. Ortoleva for stimulating discussions. The research reported in this paper is supported, in part, by the U.S. Department of Energy under Contract No. DE-AS05-81ER10947 and by the Belgian government concerted Action program. V.A. is Research Assistant at the National Fund for Scientific Research (Belgium).

Appendix

We give here a derivation of (14) of section 3. Let $X_0(r)$ denote the initial condition of the problem defined by (6a) in an infinite system. The formal solution of the equation can be written

$$X(r,t) = \exp\left(\frac{d}{dr}D(r)\frac{d}{dr}t\right)X_0(r) \quad (A1)$$

The exponential operator has to be understood as an infinite series

$$\exp\left(\frac{d}{dr}D(r)\frac{d}{dr}t\right) = 1 + \frac{d}{dr}D\frac{d}{dr}t + \frac{1}{2}\frac{d}{dr}D\frac{d^2}{dr^2}D\frac{d}{dr}t^2 + \dots \quad (A2)$$

We are now in a position to evaluate the term $\langle D(r) \partial X / \partial r \rangle$ appearing in (11). Since $D(r) = D_0 + D_1(r)$, we have two contributions. The deterministic part leads trivially to

$$\left\langle D_0 \frac{\partial X}{\partial r} \right\rangle = D_0 \frac{\partial X}{\partial r} \quad (A3)$$

To compute the second contribution, we make use of Novikov's theorem already quoted in section 3. From (A1), we get

$$\left\langle D_1(r) \frac{\partial X}{\partial r} \right\rangle = \int dr' g(r-r') \frac{\partial}{\partial r} \frac{\partial}{\partial r'} \delta(r-r') \frac{\partial}{\partial r} t \langle X(r',t) \rangle \quad (A4)$$

where we used the standard techniques of functional derivation.¹⁷ Integrating (A4) twice by parts leads to

$$\left\langle D_1(r) \frac{\partial X}{\partial r} \right\rangle = g''(0)t \frac{\partial}{\partial r} \langle X(r,t) \rangle \quad (A5)$$

(18) Ortoleva, P.; Chadam, J.; Merino, E.; Sen, A. *Am. J. Sci.* **1988**, *287*, 1008.

(19) Dewel, G.; Borckmans, P. *Phys. Lett.*, in press.