J. Fluid Mech. (1978), *vol.* 85, *part* 2, *pp.* 233–240
Printed in Great Britain

Random advection of chemically reacting species

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(Received 19 January 1977 and in revised form 6 May 1977)

In the absence of molecular diffusion there exists a space-independent transformation which transforms the probability density of dynamically passive scalars undergoing chemical reaction and advection into the probability density of scalar fields undergoing advection alone. In two well-known limits the equation for the probability density of non-reacting scalars is linear and parabolic in physical space. In such cases it is shown that the equation for the probability density of reacting scalars is likewise linear and parabolic in physical space, although hyperbolic in concentration space. The general solution of such an equation is obtained and the particular case of a second-order, decaying, single-species reaction is displayed.

1. Introduction

Probability density formulations of turbulence and turbulent transport have begun to receive more attention over the last decade, especially since Monin (1967) and Lundgren (1967) showed how to derive the equation for the multi-point density from the conservation equations of the velocity field and any advected species. Ievlev (1970) gives perhaps the most general statement of this methodology using the approach of Monin and Yaglom. Dopazo (1973), in the first specific application of the method to flows with advected chemically reacting species, noted that the species production-rate terms were closed in the probability density formulation and suggested that this may give the method a significant advantage over the traditional moment formulation, especially for nonlinear or temperature-sensitive reactions.

The study of very rapid reactions by Toor (1962) led naturally to the use of probability densities rather than moments in order to express an analogy between the advection of a dynamically passive reacting species and the advection of a passive contaminant. More recent papers by Lin & O'Brien (1974) and Bilger (1976) have extended this concept and shown that it can be a fruitful way to study reactive flows.

In this paper we display another advantage of the probability density method; namely, in the absence of molecular diffusion, there exists a transformation from the probability density associated with an advection–nonlinear reaction equation to the probability density of a scalar field undergoing advection alone. The advection problem has been the focus of many studies ranging from formal limit theorems (see Popanicolaou & Kohler (1974) and references therein) through the exact white-noise velocity solution of Kraichnan (1968) to the influential asymptotic results of Taylor (1921). Multi-point studies of the same problem continue to play a major role in clarifying the statistical geometry of lines and surfaces in a turbulent fluid (Kraichnan 1974).

It is our purpose here to relate the transformation mentioned above to the existing literature on single-point passive-scalar transport so that the statistical properties of the former may be deduced from the known results for the latter when molecular diffusion of the scalar is not directly important.

Unfortunately, molecular diffusion is rarely unimportant in turbulent diffusion problems (Batchelor & Townsend 1956) and the present inability to treat it satisfactorily by probability density methods (Hill 1976), or others (Saffman 1960), is a major barrier to progress, especially for reactive flows. For fast, diffusion-controlled reactions the structure of reaction zones and therefore the evolution of a reaction depends crucially on the role of molecular diffusion (Bilger 1976). In such a case the transformation employed here will not be valid. For premixed reactants of moderate to slow rate compared with the advection time, where large-scale spatial inhomogeneities predominate, it may be directly applicable. For example, in meteorological applications the apparently diffusive nature of turbulence often overwhelms true molecular diffusion, and if there exists a cloud of premixed reactants of moderate rate for which the ambient air is chemically inert, its transport and dilution by atmospheric turbulence may be adequately represented by this result.

In two limiting cases described in § 3 our result takes the form of an eddy-diffusivity type of term for the advection. It is therefore connected with previous *ad hoc* approximations for turbulent transport of the probability density (Kuznetsov & Frost 1973; O'Brien, Meyers & Benkovitz 1976) and gives them validity under the conditions of § 3. Furthermore, in the literature on non-diffusive transport of scalar species, there exist several studies of chemically reacting species undergoing diffusion by continuous movements (Corrsin 1968; Riley 1973). This paper also presents an Eulerian description of that situation for an arbitrary set of reactions.

2. The advection–reaction probability density equation

Consider the system of initial-value problems represented by the mass conservation equations for each of m species:

$$\left.\begin{aligned}\Gamma^i_t(\mathbf{x},t)+\mathbf{u}(\mathbf{x},t).\nabla\Gamma^i(\mathbf{x},t) &= R^i[\Gamma^1(\mathbf{x},t),\dots\,\Gamma^m(\mathbf{x},t)],\\ \Gamma^i(\mathbf{x},0) &= f^i(\mathbf{x}),\end{aligned}\right\}\quad i=1,\dots,m, \qquad (2.1)$$

where $\Gamma^i(\mathbf{x},t)$ is the concentration of the ith dynamically passive species at $(\mathbf{x},t)$, $\mathbf{u}(\mathbf{x},t)$ is the advecting, random, velocity field, $f(\mathbf{x})$ is the initial (deterministic) concentration and R^i represents the production-rate term for the ith species and is a deterministic function of the m variables $\Gamma^1,\dots,\Gamma^m$. To include non-isothermal (but still dynamically passive) effects we note that Γ^k might be an enthalpy and R^k the corresponding production-rate term (Dopazo 1973).

We seek to determine the probability density $P(\mathbf{x},t,\hat{\mathbf{\Gamma}}) = P(\mathbf{x},t,\hat{\Gamma}^1,\ldots,\hat{\Gamma}^m)$ of the process defined by (2.1) and to achieve this the fine-grained density

$$\rho(\mathbf{x},t,\hat{\mathbf{\Gamma}}) = \delta[\mathbf{\Gamma}(\mathbf{x},t)-\hat{\mathbf{\Gamma}}]$$

is introduced (Lundgren 1967). $\rho(\mathbf{x},t)$ is a measure on $\hat{\mathbf{\Gamma}}$ space and as such it satisfies the differential equation (Brissaud & Frisch 1974)

$$\rho_t+\mathbf{u}.\nabla_{\mathbf{x}}\rho+\nabla_{\hat{\Gamma}}.(\mathbf{R}\rho) = 0, \tag{2.2}$$

where $$\nabla_{\mathbf{x}} = \left(\frac{\partial}{\partial x_1},\frac{\partial}{\partial x_2},\frac{\partial}{\partial x_3}\right),\quad \nabla_{\hat{\Gamma}} = \left(\frac{\partial}{\partial\hat{\Gamma}^1},\ldots,\frac{\partial}{\partial\hat{\Gamma}^m}\right).$$

We introduce the fine-grained density ρ^* for the non-reacting advection equation. Let $\mathbf{\Gamma}^*$ be the solution of

$$\left.\begin{aligned}\mathbf{\Gamma}^*_t+\mathbf{u}.\nabla_{\mathbf{x}}\mathbf{\Gamma}^* &= 0,\ t\geqslant 0,\\ \mathbf{\Gamma}^*(\mathbf{x},0) &= \mathbf{f}(\mathbf{x}).\end{aligned}\right\} \tag{2.3}$$

Then $\rho^*(\mathbf{x},t,\hat{\mathbf{\Gamma}}) \equiv \delta[\mathbf{\Gamma}^*(\mathbf{x},t)-\hat{\mathbf{\Gamma}}]$ satisfies

$$\rho^*_t+\mathbf{u}.\nabla_{\mathbf{x}}\rho^* = 0,\quad t\geqslant 0, \tag{2.4}$$

and $\rho = \rho^*$ at $t = 0$.

Define a linear operator A such that $Ag \equiv -\nabla_{\hat{\Gamma}}.(\mathbf{R}g)$. Then, since A is independent of $\mathbf{x}$ and t,

$$\partial(e^{tA}\rho^*)/\partial t = A(e^{tA}\rho^*)+e^{tA}\rho^*_t = -\nabla_{\hat{\Gamma}}.[\mathbf{R}(e^{tA}\rho^*)]-\mathbf{u}.\nabla_{\mathbf{x}}(e^{tA}\rho^*). \tag{2.5}$$

Since $\rho = \rho^* = e^{tA}\rho^*$ when $t = 0$, (2.2) and (2.5) imply that $\rho = e^{tA}\rho^*$ for all $t\geqslant 0$. Let angle brackets symbolize the ensemble average and define $P = \langle\rho\rangle$ and $P^* = \langle\rho^*\rangle$. Then, since A is deterministic,

$$P = e^{tA}\langle\rho^*\rangle = e^{tA}P^*. \tag{2.6}$$

The transformation (2.6) represents a formal solution for the reactive advective probability density P in terms of solutions P^* to the non-reactive advective problem with the same random velocity field and the same initial fine-grained density $\rho(\mathbf{x},0,\hat{\mathbf{\Gamma}})$. The first important question to ask is whether solutions to P^* exist or can be obtained. This matter is considered in the following pages. The second question should be concerned with the usefulness of the operator form (2.6) in solving turbulent advection of species which react according to complicated kinetic schemes. When P^* satisfies an evolution equation of the form $\partial P^*/\partial t+LP^* = 0$, where L is a linear operator involving only operations in physical space (i.e. no differentiation in time or concentration space), then P satisfies the equation

$$\partial P/\partial t+LP+\nabla_{\hat{\Gamma}}.(\mathbf{R}P) = 0. \tag{2.7}$$

This follows from (2.6) using a calculation similar to (2.5). In the next section it is shown that P^* satisfies a linear equation of the type $\partial P^*/\partial t+LP^* = 0$ when (*a*) the turbulence is homogeneous and the time scale is much larger than the Lagrangian time scale of the turbulence or (*b*) the velocity-field correlation time is very short compared with the concentration-field circulation time. In §4 we make use of (2.7) to calculate P explicitly in these two cases.

Alternatively, one can view (2.6) as a numerical procedure for calculating P from a P^* known empirically or otherwise. The question of convergence of the series

$e^{tA} = \Sigma(tA)^n/n!$ is not trivial. It is briefly considered in Meyers, O'Brien & Scott (1977) with particular application to a lognormal distribution P^*, for which $e^{tA}P^*$ is shown to have a finite radius of convergence in both t and $\hat{\Gamma}$. In addition a technique is described for calculating $e^{tA}P^*$ for all values of t and $\hat{\Gamma}$, in spite of the finite radius of convergence.

3. Probability density solutions of the advection equations

The random-walk limit

An important asymptotic result for the probability density of the displacement of a single fluid particle in homogeneous stationary turbulence has been given by Batchelor (1952) and Roberts (1961), both of whom extended the pioneering analysis of Taylor (1921).

The probability density describing a process in which a fluid particle which is at $\mathbf{a}$ at time t_0 will be at $\mathbf{x}$ at time t is

$$p(\mathbf{x}, t;\ \mathbf{a}, t_0) = \langle \delta[\mathbf{x} - \mathbf{r}(\mathbf{a}, t)] \rangle,$$

where $\mathbf{r}(\mathbf{a}, t)$ describes the trajectory of the particle and $\mathbf{r}(\mathbf{a}, t_0) = \mathbf{a}$. Employing only mild constraints on the velocity-field statistics, Batchelor has shown that $p(\mathbf{x}, t;\ \mathbf{a}, t_0)$ is asymptotically normal for times t much longer than the Lagrangian time scale of the advecting velocity field and he has computed the general particle-displacement covariance tensor, which is asymptotically linear in time.

The importance of $p(\mathbf{x}, t;\ \mathbf{a}, t_0)$ for the purposes of this note is that it can be directly related to $P^*(\mathbf{x}, t;\ \hat{\boldsymbol{\Gamma}})$ in the following way:

$$P^*(\mathbf{x}, t, t_0;\ \hat{\boldsymbol{\Gamma}}) = \int P^*(\mathbf{a}, t_0;\ \hat{\boldsymbol{\Gamma}})\, p(\mathbf{x}, t;\ \mathbf{a}, t_0)\, d\mathbf{a}, \tag{3.1}$$

where $P^*(\mathbf{a}, t_0;\ \hat{\boldsymbol{\Gamma}}) = \langle \delta[\hat{\boldsymbol{\Gamma}} - \boldsymbol{\Gamma}(\mathbf{a}, t_0)] \rangle$ and $\boldsymbol{\Gamma}(\mathbf{a}, t_0)$ is the initial spatial distribution of $\boldsymbol{\Gamma}$, which may be random but must be statistically independent of the advecting field $\mathbf{u}$. For simplicity the dependence of the left-hand side of (3.1) on the initial time t_0 will be suppressed.

The proof of (3.1) uses the general relationship (O'Brien 1963; Hill 1976)

$$P^*(\mathbf{x}, t;\ \hat{\boldsymbol{\Gamma}}) = \int \langle \delta[\hat{\boldsymbol{\Gamma}} - \boldsymbol{\Gamma}(\mathbf{a}, t)]\, \delta[\mathbf{x} - \mathbf{r}(\mathbf{a}, t)] \rangle\, d\mathbf{a}.$$

In Lagrangian co-ordinates the species advection equation (2.1) becomes

$$\partial \Gamma^i(\mathbf{a}, t)/\partial t = 0.$$

Hence $P^*(\mathbf{x}, t;\ \hat{\boldsymbol{\Gamma}}) = \int \langle \delta[\hat{\boldsymbol{\Gamma}} - \boldsymbol{\Gamma}(\mathbf{a}, t_0)]\, \delta[\mathbf{x} - \mathbf{r}(\mathbf{a}, t)] \rangle\, d\mathbf{a}$.

When $\boldsymbol{\Gamma}(\mathbf{a}, t_0)$ is statistically independent of the advecting field $\mathbf{u}$, (3.1) follows and P^* can be computed from given initial concentration data and the behaviour of $p(\mathbf{x}, t;\ \mathbf{a}, t_0)$.

Several proposals can be found in the literature for evolution equations describing the behaviour of $\bar{p}(\mathbf{x}, t;\ \mathbf{a}, t_0)$ where $\bar{p}$ is an approximation to p. The direct-interaction technique (Roberts 1961) produces the following result when the advecting field $\mathbf{u}(\mathbf{x}, t)$ is incompressible and its mean $\langle \mathbf{u}(\mathbf{x}, t) \rangle$ vanishes:

$$\frac{\partial}{\partial t} \bar{p}(\mathbf{x}, t;\ \mathbf{a}, t_0) = \int_{t_0}^{t} dt' \int d\mathbf{x}'\, U_{ij}(\mathbf{x}, t;\ \mathbf{x}', t')\, \frac{\partial}{\partial x_i} \bar{p}(\mathbf{x}, t;\ \mathbf{x}', t_0)\, \frac{\partial}{\partial x'_j} \bar{p}(\mathbf{x}', t';\ \mathbf{a}, t_0), \tag{3.2}$$

where $U_{ij}(\mathbf{x}, t;\ \mathbf{x}', t') = \langle u_i(\mathbf{x}, t)\, u_j(\mathbf{x}', t') \rangle$.

Equation (3.2) is nonlinear, as is typical of all other serious approximations (e.g. Bourret 1960), so it follows that neither $P^*(\mathbf{x}, t; \hat{\mathbf{\Gamma}})$ nor $P(\mathbf{x}, t; \hat{\mathbf{\Gamma}})$ will in general satisfy an equation analogous to (3.2). In homogeneous flows for times very large compared with the time formed from the turbulence macroscale l_0 and the r.m.s. fluid velocity v_0, i.e. $t \gg l_0 v_0^{-1}$, Batchelor & Townsend (1956) have shown that

$$p(\mathbf{x}, t;\, \mathbf{a}, t_0) = p(\mathbf{x}-\mathbf{a}, t-t_0)$$

is asymptotically Gaussian.

The same property holds for the homogeneous version of (3.2) as was shown by Roberts (1961), who also proved that, in the limit $t \gg l_0 v_0^{-1}$, (3.2) becomes

$$\frac{\partial \overline{p}}{\partial t}(\mathbf{x}, t;\, \mathbf{a}, t_0) = K_{ij}^{\infty} \frac{\partial^2}{\partial x_i\, \partial x_j} \overline{p}(\mathbf{x}, t;\, \mathbf{a}, t_0),$$

where
$$K_{ij}^{\infty} = \int_0^{\infty} dt' \int d\mathbf{y}\, p(\mathbf{y}, t')\, U_{ij}(\mathbf{y}, t')$$

is a constant eddy diffusivity. In this limit, from (3.1), P^* satisfies the linear equation

$$\partial P^*/\partial t + K_{ij}^{\infty}\, \partial^2 P^*/\partial x_i\, \partial x_j = 0$$

and P obeys (2.7) with L given by $K_{ij}^{\infty}\, \partial^2/\partial x_i\, \partial x_j$.

The rapid-fluctuation limit

The limit theorems mentioned in the introduction (see Papanicolaou & Kohler 1974) lead directly to an equation for P^*. Here we shall be content to describe the main result; for details, one may refer to Meyers *et al.* (1977). Consider the initial-value problem for the following mass conservation equation for one species:

$$\left.\begin{aligned} \Gamma_t + \epsilon \mathbf{u}.\nabla\Gamma &= 0 \quad t \geqslant 0, \\ \Gamma(\mathbf{x}, 0) &= f(\mathbf{x}), \end{aligned}\right\} \tag{3.3}$$

where ϵ is a small positive parameter and (for convenience) $\langle \mathbf{u} \rangle \equiv 0$. As ϵ tends to zero, the velocity-field correlation time becomes infinitely short compared with the concentration-field circulation time, and (3.3) is therefore related to Kraichnan's (1968) condition for an exact solution for the scalar correlation function in a homogeneous field with white-noise advection. To derive a limit theorem, one must in addition impose a technical *mixing condition* on the velocity field $\mathbf{u}$ such that $\mathbf{u}(\mathbf{x}, t+\tau)$ and $\mathbf{u}(\mathbf{y}, t)$ become independent sufficiently rapidly as $\tau \to \infty$ for all $\mathbf{x}$ and $\mathbf{y}$ (see the references above for details). The limit theorem is stated in terms of the solution $\overline{\Gamma}$ of the initial-value problem for the following *deterministic* scalar diffusion equation:

$$\left.\begin{aligned} \overline{\Gamma}_t &= \epsilon^2[(\alpha_{ij}\overline{\Gamma}_{,i})_{,j} - \beta_k \overline{\Gamma}_{,k}], \quad t \geqslant 0, \\ \overline{\Gamma}(\mathbf{x}, 0) &= f(\mathbf{x}), \end{aligned}\right\} \tag{3.4}$$

where the notation $\overline{\Gamma}_{,i}$ means $\partial\overline{\Gamma}/\partial x_i$, for example, and the summation convention holds. The coefficients α_{ij} and β_k are given by the integral scales of the correlation functions:

$$\left.\begin{aligned} \alpha_{ij}(\mathbf{x}) &= 2\tfrac{1}{2}\int_0^{\infty} \langle u_i(\mathbf{x}, t)\, u_j(\mathbf{x}, 0)\rangle\, dt, \\ \beta_k(\mathbf{x}) &= 2\tfrac{1}{2}\int_0^{\infty} \langle u_k(\mathbf{x}, t)\, \nabla.\mathbf{u}(\mathbf{x}, 0)\rangle\, dt. \end{aligned}\right\} \tag{3.5}$$

Finally, we come to the *limit theorem*, namely that, on time scales proportional to ϵ^{-2},

$$\lim_{\epsilon \to 0} |\langle \Gamma \rangle - \overline{\Gamma}| = 0. \tag{3.6}$$

Here we have assumed that the velocity field $\mathbf{u}$ is statistically stationary because the limit theorem in the non-stationary case is much more complicated.

Using the fact that $P^* = \langle \rho^* \rangle$, we can obtain a limit theorem for P^* by analogy with the above results. Namely, in the limit $\epsilon \to 0$ (or, equivalently, as the velocity field approaches the time-correlation narrowing condition of white noise), P^* tends to the solution of the initial-value problem

$$\left.\begin{aligned} P^*_t - \epsilon^2[(\alpha_{ij} P^*_{,i})_{,j} - \beta_k P^*_{,k}] = 0, \quad t \geqslant 0, \\ P^*(\mathbf{x}, 0; \hat{\mathbf{\Gamma}}) = \delta[\mathbf{f}(\mathbf{x}) - \hat{\mathbf{\Gamma}}]. \end{aligned}\right\} \tag{3.7}$$

Although the results above used deterministic initial data $\mathbf{f}(\mathbf{x})$, it can be shown (Meyers *et al.* 1977) that the above limit theorem remains valid if $\mathbf{f}(\mathbf{x})$ is itself random but statistically independent of the advection velocity $\mathbf{u}$. The initial data for P^* then become the probability density for the initial data $\mathbf{f}(\mathbf{x})$. Finally, from (3.7), it follows in this limit that P again satisfies (2.7) with LP given by

$$LP = -\epsilon^2 \left[\frac{\partial}{\partial x_j} \left(\alpha_{ij} \frac{\partial P}{\partial x_i} \right) - \beta_k \frac{\partial P}{\partial x_k} \right].$$

4. Solution of the equation for the probability density

We may summarize in the following way. Given initial data which are possibly non-deterministic (but statistically independent of $\mathbf{u}$) with probability density $Q(\mathbf{x}, \hat{\mathbf{\Gamma}}_0)$, the probability density $P(\mathbf{x}, t, \hat{\mathbf{\Gamma}})$ for the solution $\mathbf{\Gamma}$ of (2.1) satisfies, in both the limits described in § 3,

$$\left.\begin{aligned} P_t - a_{ij} P_{,ij} - b_k P_{,k} + \nabla_{\hat{\mathbf{\Gamma}}} . (\mathbf{R} P) = 0, \quad t \geqslant 0, \\ P = Q, \quad t = 0, \end{aligned}\right\} \tag{4.1}$$

where the meaning of a_{ij} and b_k depends on the limit being invoked.

Equation (4.1) preserves the segregated-species results for very rapid reaction in the absence of molecular diffusion, for example those derived by O'Brien (1971) for the case of two-species, one-step reactions. In particular, it yields limit solutions quite different from those obtained by approximating the concentrations in the production-rate terms by their mean values.

The probability density evolves in both physical space and concentration space. These two effects proceed simultaneously but, because molecular diffusion has been neglected, they are independent of each other except for sharing the initial conditions. This suggests that (4.1) may be best solved by separating the behaviour in the two spaces and relating each to its state at the initial time when $P(\mathbf{x}, t, \hat{\Gamma})$ is described by the initial data $Q(\mathbf{x}, \hat{\Gamma}_0)$.

For the physical-space solution we suppose that we possess a Green's kernel $K(\mathbf{x}, \mathbf{y}, t)$ for the homogeneous problem

$$\left.\begin{aligned} F_t(\mathbf{x}, t) - a_{ij}(\mathbf{x}, t) F_{,ij}(\mathbf{x}, t) - b_k F_{,k}(\mathbf{x}, t) = 0, \quad t \geqslant 0, \\ F(\mathbf{x}, 0) = f(\mathbf{x}), \end{aligned}\right\} \tag{4.2}$$

i.e.

$$F(\mathbf{x}, t) = \int K(\mathbf{x}, \mathbf{y}, t) f(\mathbf{y})\, d\mathbf{y}.$$

For the concentration-space behaviour we adopt a Lagrangian description of the reactive process:

$$\left.\begin{aligned}\dot{\hat{\mathbf{\Gamma}}}(t;\hat{\mathbf{\Gamma}}_0) &= \mathbf{R}[\hat{\mathbf{\Gamma}}(t;\hat{\mathbf{\Gamma}}_0)], \quad t \geqslant 0,\\ \hat{\mathbf{\Gamma}}(0;\hat{\mathbf{\Gamma}}_0) &= \hat{\mathbf{\Gamma}}_0.\end{aligned}\right\} \tag{4.3}$$

If $P(\mathbf{x}, t, \hat{\mathbf{\Gamma}})$ is the solution of (4.1) with initial data Q, we can define

$$F(\mathbf{x}, t; \hat{\mathbf{\Gamma}}_0) \equiv P[\mathbf{x}, t, \hat{\mathbf{\Gamma}}(t;\hat{\mathbf{\Gamma}}_0)]$$

and straightforward use of (4.1) and (3.4) gives

$$\begin{aligned}F_t - a_{ij}F_{,ij} - b_kF_{,k} &= P_t + \dot{\hat{\mathbf{\Gamma}}}.\nabla_{\hat{\mathbf{\Gamma}}}P - a_{ij}P_{,ij} - b_kP_{,k}\\ &= -(\nabla_{\hat{\mathbf{\Gamma}}}.\mathbf{R})P = -(\nabla_{\hat{\mathbf{\Gamma}}}.\mathbf{R})F.\end{aligned} \tag{4.4}$$

Now using the Green's kernel for (4.2), it follows that the solution of (4.4) is

$$F(\mathbf{x}, t; \hat{\mathbf{\Gamma}}_0) = \exp\left\{\int_0^t -(\nabla_{\hat{\mathbf{\Gamma}}}.\mathbf{R})\,[\hat{\Gamma}(s;\,\hat{\Gamma}_0)]\,ds\right\}\int K\mathbf{x}, \mathbf{y}, t)\,Q(\mathbf{y}, \hat{\Gamma}_0)\,dy.$$

If we invert the relation $\hat{\mathbf{\Gamma}} = \hat{\mathbf{\Gamma}}(t;\hat{\mathbf{\Gamma}}_0)$ to obtain $\hat{\mathbf{\Gamma}}_0 = \hat{\mathbf{\Gamma}}_0(\hat{\mathbf{\Gamma}};t)$ we may write the solution of (4.1) as

$$P(\mathbf{x}, t; \hat{\mathbf{\Gamma}}) = \exp\left\{\int_0^t -(\nabla_{\hat{\mathbf{\Gamma}}}\cdot\mathbf{R})\,[\hat{\mathbf{\Gamma}}(s;\hat{\mathbf{\Gamma}}_0(\hat{\mathbf{\Gamma}};t))]\,ds\right\}\int K(\mathbf{x}, \mathbf{y}, t)\,Q[\mathbf{y}, \hat{\mathbf{\Gamma}}_0(\hat{\mathbf{\Gamma}};t)]\,dy. \tag{4.5}$$

We now give a closed-form solution for $P(\mathbf{x}, t; \hat{\mathbf{\Gamma}})$. Let $m = 1$ (one species) and let $R(\hat{\Gamma}) = -k\hat{\Gamma}^2$. Then

$$\hat{\Gamma}(t;\hat{\Gamma}_0) = 1/(\hat{\Gamma}_0^{-1} + kt), \quad \hat{\Gamma}_0 = 1/(\hat{\Gamma}^{-1} - kt).$$

Therefore

$$\nabla_{\hat{\mathbf{\Gamma}}}.\mathbf{R} = -2k\hat{\Gamma}$$

and

$$\int_0^t -(\nabla_{\hat{\mathbf{\Gamma}}}.\mathbf{R})\,[\hat{\mathbf{\Gamma}}(s;\,\hat{\mathbf{\Gamma}}_0(\hat{\mathbf{\Gamma}};\,t))]\,ds = \ln{(1 + kt\hat{\Gamma}_0)^2} = \ln{(1 - kt\hat{\Gamma})^{-2}}.$$

Thus

$$P(\mathbf{x}, t, \hat{\Gamma}) = (1 - kt\hat{\Gamma})^{+2}\int K(\mathbf{x}, \mathbf{y}, t)\,Q[\mathbf{y}, \hat{\Gamma}/(1 - kt\hat{\Gamma})]\,dy. \tag{4.6}$$

The zero-diffusivity case for a single-species reaction was examined by Hill (1970). Equations (4.5) and (4.6) may be considered as the proper form, in the two limits of §3, of his formal expression [his equation (4)] for the single-point probability density. The invariance properties discussed by Hill are therefore preserved in these limits. It also follows that an eddy-diffusivity representation of turbulent advection of scalar probability density will satisfy his zero-diffusivity invariance requirements.

The authors would like to thank R. H. Kraichnan for his valuable suggestions. This work has been supported by ERDA under grant no. EY-76-C-02-0016 and was performed at the Brookhaven National Laboratory, to which E. E. O'Brien is a consultant.

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