Asymptotic Solutions of Hopf's Equation for Turbulent Chemical Reactions

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Hopf's formalism is extended to chemically reactive turbulent systems, and weak mixing and convective mixing asymptotic forms are considered. The former recovers Corrsin's isotropic decay law for an isothermal first-order, irreversible reaction; the latter extends Hopf's result to equipartition of mechano-chemical energy.

Big whirls have little whirls,
that feed on their velocity;
and little whirls have lesser whirls,
and so on to viscosity.

L. F. Richardson (*1*)

If Richardson's jingle truly renders the poetry of the energy transfer from one mode to another in turbulent flow, then valuable information about large eddies can be obtained from the final period of decay. The observation that the energy spectrum at small wave numbers undergoes little modulation during decay indicates that for long times these large eddies must ultimately supply the energy to sustain what has been called "weak turbulence" (*2*). The assumption that inertial forces are small relative to viscous effects leads to a rather spurious kind of turbulence, but asymptotic weak turbulence nevertheless affords an opportunity to treat a tractable decay problem which has received experimental verification (*3*).

Lewis and Kraichnan (*4*) recovered the theory of weak turbulence by solving a space-time generalization of Hopf's functional differential equation (*5*) for the asymptotic zero Reynolds number case. This solution, together with Hopf's original exact solution for inviscid dynamics, are the only explicit results which have been extracted from Hopf's functional differential equation, although several attempts have been made (*6*). The purpose of this paper is to recover the corresponding weak-mixing and convective-mixing asymptotic cases of turbulent chemical reactions studied by Corrsin (*7*). The intent here is to further demonstrate an element of naturalness of a Hopf formulation for any statistical problem associated with a continuous medium.

HOPF EQUATION FOR CHEMICALLY REACTIVE TURBULENCE

The Navier-Stokes equations and the chemical species continuity equations in the forms

$$\frac{\partial \mathbf{u}}{\partial t} = -N_{Re}\,[\underset{\approx}{1} + \nabla\Delta^{-1}\nabla]\nabla : \mathbf{uu} + \Delta\mathbf{u} \qquad (1)$$

$$\frac{\partial c}{\partial t} = -N_{Pe}\,\mathbf{u}\cdot\nabla c + \Delta c - N_{Da}c^n \qquad (2)$$

have been made dimensionless, with N_{Re}, N_{Pe}, and N_{Da} the familiar Reynolds, Péclet, and Damköhler numbers, and the solenoidality of $\mathbf{u}$ has been used to eliminate the pressure. Following Hopf (*5, 6*) we suppose that Equations (1) and (2) have the requisite properties, in particular that there are a pair of Hilbert spaces $\mathcal{H}^1$ and $\mathcal{H}^2$ within which a pair of semigroups $T_1{}^t$ and $T_{2,\mathbf{u}}{}^t$ map initial velocity and concentration fields $\mathbf{u}_0\epsilon\Omega_0{}^1$ and $c_0\epsilon\Omega_0{}^2$ into their instantaneous values. Thus, $\mathbf{u} = T_1{}^t\mathbf{u}_0$ and $c = T_{2,\mathbf{u}}{}^t c_0$ represent solutions of the forced convection problem with Equations (1) and (2) becoming identities for all t upon substitution. The explicit notation $T_{2,\mathbf{u}}{}^t$ emphasizes that for any admissible velocity field, that is, satisfying Equation (1), there is supposed an admissible concentration field, that is, satisfying Equation (2), a supposition consistent with Hopf's assumption regarding $T_1{}^t$, although both exceed what has been rigorously proved.

Probability measures $\mu_0{}^1(\mathbf{u}_0)$, $\mu^1(\mathbf{u})$ and $\mu_0{}^2(c_0)$, $\mu^2(c)$ and integrals over the spaces $\Omega_0{}^1$, $\mathcal{H}^1$ and $\Omega_0{}^2$, $\mathcal{H}^2$ are likewise presumed. Then the characteristic functional for the velocity field $M[\mathbf{v}; t]$ is defined in terms of the probability density functional $f[\mathbf{u}; t]$ by

$$M[\mathbf{v}; t] = \int_{\mathcal{H}^1} \exp\{i[\mathbf{v}, \mathbf{u}]\}\, f[\mathbf{u}; t]\, d\mu^1,$$

which can be converted to an integral over the space $\Omega_0{}^1$ of initial conditions by introducing

$$f[\mathbf{u}; t] = \int_{\Omega_0{}^1} \delta[\mathbf{u} - T_1{}^t\,\mathbf{u}_0] f[\mathbf{u}_0]\, d\mu_0{}^1 \,. \qquad (3)$$

Thus

$$M[\mathbf{v}; t] = \int_{\Omega_0{}^1}\int_{\mathcal{H}^1} \exp\{i[\mathbf{v}, \mathbf{u}]\}$$
$$\delta[\mathbf{u} - T_1{}^t\mathbf{u}_0] f[\mathbf{u}_0] d\mu^1 d\mu_0{}^1$$
$$= \int_{\Omega_0{}^1} \exp\{i[\mathbf{v}, T^t\mathbf{u}_0]\} f[\mathbf{u}_0] d\mu_0{}^1\,, \qquad (4)$$

which satisfies [compare Hopf (*5*)]

$$\frac{\partial M}{\partial t}[\mathbf{v}; t] = \left[\mathbf{v}, \Delta\frac{\delta}{\delta\mathbf{v}}M\right]$$
$$+ iN_{Re}\left[\mathbf{v}, (\underset{\approx}{1} - \nabla\Delta^{-1}\nabla)\nabla : \frac{\delta^2}{\delta\mathbf{v}^2}M\right] \qquad (5)$$

Extension to a binary fluid mixture undergoing an *n*th order irreversible reaction requires introduction of the conditional probability density functional

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$$f[c|\mathbf{u};t] = \int_{\Omega_0{}^2}\int_{\Omega_0{}^1} \delta[c - T_{2,\mathbf{u}}{}^t c_0]\delta[\mathbf{u} - T_1{}^t\mathbf{u}_0] \\ f[c_0, \mathbf{u}_0] \times d\mu_0{}^1\, d\mu_0{}^2 \qquad (6)$$

with the corresponding characteristic functional

$$M[b|\mathbf{v};t] = \int_{\mathcal{H}^2}\int_{\mathcal{H}^1} \exp\{i[b, c] \\ + i[\mathbf{v}, \mathbf{u}]\} f[c|\mathbf{u};t]d\mu^1\, d\mu^2 \\ = \int_{\Omega_0{}^2}\int_{\Omega_0{}^1} \exp\{i[b, T_{2,\mathbf{u}}{}^t c_0] + i[\mathbf{v}, T_1{}^t\mathbf{u}_0]\} f[c_0, \mathbf{u}_0] \\ \times d\mu_0{}^1\, d\mu_0{}^2 . \qquad (7)$$

The partial time derivative may then be written

$$\frac{\partial M}{\partial t}[b|\mathbf{v};t] = \int_{\Omega_2{}^0}\int_{\Omega_0{}^1} \left\{ i\left[b, \frac{\partial}{\partial t} T_{2,\mathbf{u}}{}^t c_0) \right] \right. \\ \left. + i\left[\mathbf{v}, \frac{\partial}{\partial t}(T_1{}^t\mathbf{u}_0)\right] \right\} \times \exp\{i[b, T_{2,\mathbf{u}}{}^t c_0] \\ + i[\mathbf{v}, T_1{}^t\mathbf{u}_0]\} \times f[c_0, \mathbf{u}_0]\mathrm{d}\mu_0{}^1\, \mathrm{d}\mu_0{}^2 ,$$

and introduction of Equations (1), (2), and (6), together with commutation of ensemble averaging and of spatial differentiation and integration in the form of

$$\int_{\mathcal{H}^2}\int_{\mathcal{H}^1} i(b, \Delta c) \exp\{i[b, c] \\ + i[\mathbf{v}, \mathbf{u}]\} f[c|\mathbf{u}:t]d\mu^1\, d\mu^2 = \left[b, \Delta \frac{\delta}{\delta b} M \right]$$

and similar relations involving other Fréchet derivatives of the characteristic functional, yields

$$\frac{\partial}{\partial t} M[b|\mathbf{v};t] = \left[b, \Delta \frac{\delta}{\delta b} M \right] + i N_{Da} \left[b, \frac{\delta^n}{\delta b^n} M \right] \\ + i N_{Pe} \left[b, \nabla \cdot \frac{\delta^2}{\delta b\, \delta \mathbf{v}} M \right] + \left[\mathbf{v}, \Delta \frac{\delta}{\delta \mathbf{v}} M \right] \\ + i N_{Re} \left[\mathbf{v}, (\underset{\approx}{1} - \nabla\Delta^{-1}\nabla)\nabla : \frac{\delta^2}{\delta \mathbf{v}^2} M \right] . \qquad (8)$$

Equation (8) is the extension of the Hopf formalism to an isothermal binary system undergoing an *n*th order irreversible reaction and contains Hopfs' Equation (5) as the special case b equal to zero. The temporal evolution of the characteristic functional for the turbulent velocity and concentration fields is described by Equation (8). It illustrates, in particular, the well recognized fact that the statistics of a passive additive scalar field cannot be determined with anything less than the full initial statistics of both fields, here as contained in $M[b|\mathbf{v};0]$; for instance, even if $\mathbf{v}$ is set to the null vector in Equation (8), $M[b|0;t]$ still depends upon $M[b|\mathbf{v};t]$ through the coupling term

$$\left[b, \nabla \cdot \frac{\delta^2}{\delta b\, \delta \mathbf{v}} M \right]\Bigg|_{\mathbf{v}=0} .$$

The onerous inertial nonlinearity of the Navier-Stokes equation becomes a second order Fréchet derivative of the characteristic functional in the Hopf formulation, with Hopf's functional partial differential equation being linear and of second order. Similarly, the *n*th order nonlinearity of the chemical reaction in the species continuity equation becomes an *n*th order Fréchet derivative in the extension, but again the functional differential equation is linear, although now instead of two independent variables there are three, b, $\mathbf{v}$ and t.

That extension (8) is of the form of a Liouville equation when written in terms of the probability density functional is demonstrated using relations such as
$i[b, \Delta c]\exp\{i[b, c] + i[\mathbf{v}, \mathbf{u}]\} f[c|\mathbf{u};t]$

$$= \frac{\delta}{\delta c}[\exp\{i[b, c] + i[\mathbf{v}, \mathbf{u}]\}, f[c|\mathbf{u};t]\Delta c] \\ - [\exp\{i[b, c] + i[\mathbf{v}, \mathbf{u}]\}, \frac{\delta}{\delta c}\{f[c|\mathbf{u};t]\Delta c\}]$$

and integrating them over the phase space $\mathcal{H}^1 \times \mathcal{H}^2$ to give

$$\frac{\partial f}{\partial t} = Lf = \int_R d\mathbf{x} \frac{\delta}{\delta c}\{(N_{Pe}\mathbf{u} \cdot \nabla c + N_{Da} c^n - \Delta c) f\} \\ + \int_R d\mathbf{x} \frac{\delta}{\delta \mathbf{u}} \cdot \{[N_{Re}(\underset{\approx}{1} + \nabla\Delta^{-1}\nabla)\nabla : \mathbf{uu} - \Delta\mathbf{u}] f\} \quad (9)$$

ASYMPTOTIC SOLUTIONS

Under the restrictive assumptions of small Péclet number and isotropy, Corrsin (7) derived a decay law for the mean square fluctuation of residual reactant undergoing an isothermal first-order, irreversible reaction. Decay is as for pure mixing except for exponential damping due to reaction

$$<\hat{c}^2> \sim \exp(-N_{Da}\, t)/t^{3/2} ,$$

in which $\hat{c}$ is the fluctuating component of an isotropic concentration field. Large Schmidt numbers for liquids, however, limit application primarily to gases.

Corrsin's decay law can be easily derived from the specialization of Equation (8) to a first order reaction in isotropic turbulence. Upon setting $\mathbf{v} = \mathbf{0}$ and neglecting the convective term, the asymptotic functional differential equation

$$\frac{\partial M}{\partial t} = \int_R d\mathbf{x}\, b\{\Delta - N_{Da}\} \frac{\delta}{\delta b} M \qquad (10)$$

results. The *m*th Fréchet derivative of (10) is

$$\frac{\partial}{\partial t}\frac{\delta^m}{\delta b^m} M = \{\Delta - N_{Da}\} \frac{\delta^m}{\delta b^m} M ,$$

and for $m = 2$, $\mathbf{x}_1 = \mathbf{x}_2$, and isotropy, Corrsin's equation for the mean squared residual concentration in the form

$$\left\{ \frac{\partial}{\partial t} - \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + N_{Da} \right\} \left(\frac{\delta^2}{\delta b^2} M \bigg|_{b=0} \right) = 0$$

results.

Hopf's equation for incompressible viscous turbulence, Equation (5), possesses a statistically stationary solution in the limit of large Reynolds number (5, 6) which is theoretically important because equipartition of mechanical energy is a touchstone in most closures (8). In what follows the extension of Hopf's formalism to include convection of a passive scalar field is shown also to have a statistically stationary infinite Reynolds number, asymptotic solution.

The steady functional equation which governs the nonlinear scrambling of the turbulence as well as the concentration is, from Equation (8),

$$\int dx \left\{ \mathbf{v} \cdot (\underset{\approx}{1} + \nabla\Delta^{-1}\nabla)\nabla : \frac{\delta^2}{\delta \mathbf{v}^2} M \right\} \\ + \frac{N_{Pe}}{N_{Re}} \int dx' \left\{ b\nabla \cdot \frac{\delta^2}{\delta b\, \delta \mathbf{v}} M \right\} = 0 . \qquad (11)$$

The first term has already been treated by Hopf in Fourier form, which also makes the second term straightforward.

In his notation, with $\tilde{\mathbf{z}}$ an arbitrary solenoidal vector field replacing v in the Fourier representation, Equation (11) may be rewritten

$$\int_{\mathbf{k}'} \frac{\delta}{\delta \tilde{z}_i(\mathbf{k}')} \left\{ \int_{\mathbf{k}''} \left[\tilde{z}_j(\mathbf{k}' + \mathbf{k}'') K_{ijk} \frac{\delta}{\delta \tilde{z}_k(\mathbf{k}'')} M + \frac{N_{Pe}}{N_{Re}} b(\mathbf{k}' + \mathbf{k}'') k_i'' \frac{\delta}{\delta b(\mathbf{k}'')} M \right] \right\} = 0\,; \quad (12)$$

the "projector" K_{ijk} is given by

$$K_{ijk} = \left(k_i'' - \frac{\mathbf{k}' \cdot \mathbf{k}''}{\mathbf{k}'^2} k_i' \right) \left(\delta_{jk} - \frac{k_j'' k_k''}{\mathbf{k}''^2} \right).$$

Equipartition of mechano-chemical energy is guaranteed by the following:

Theorem:

If $W(\psi)$, $\psi \geqq 0$ is an arbitrary function of a single variable which possesses a continuous second derivative, then

$$M = W\left(\int_{\mathbf{k}} [\tilde{\mathbf{z}}(\mathbf{k}) \cdot \tilde{\mathbf{z}}(-\mathbf{k}) + b(\mathbf{k}) b(-\mathbf{k})] \right) \quad (13)$$

satisfies Equation (12). (Here, $\tilde{\mathbf{z}}(\mathbf{k})$ and $b(\mathbf{k})$ can be normalized with the square roots of N_{Re} and N_{Pe}, respectively.)

Proof:

The functional derivative of (13) with respect to b is

$$\frac{\delta M}{\delta b(\mathbf{k}'')} = 2\,(dW/d\psi) b(-\mathbf{k}''), \quad (14)$$

and because the first term differentiates to zero with respect to b, the second term with respect to $\tilde{\mathbf{z}}$, the theorem will be proved if (14) is zero, for Hopf's original proof demonstrated the vanishing of the derivative of the first term with respect to $\tilde{\mathbf{z}}$. Substitution of (13) and (14) and manipulation then gives, for the left side of (12),

$$4(d^2W/d\psi^2) \int_{\mathbf{k}'} \int_{\mathbf{k}''} \tilde{z}_i(-\mathbf{k}') b(-\mathbf{k}'') b(\mathbf{k}' + \mathbf{k}'') k_i'',$$

which vanishes because of conservation of wave numbers upon integration, invariance of a resultant intermediate step under interchange of wave numbers, and the Fourier representation of solenoidality $\mathbf{k} \cdot \tilde{\mathbf{z}}(\mathbf{k}) = 0$. Thus, the characteristic functional (13) satisfies the stationary equation at infinite Reynolds number.

This theorem extends Hopf's now classical inviscid solution to the case of a scalar constituent convected by the turbulence. As he observed in his case, if $W(\cdot)$ corresponds to the familiar characteristic functional of an isotropic Gaussian distribution, then

$$M = \exp\left\{ -\int_{\mathbf{k}} \left[\tilde{\mathbf{z}}(\mathbf{k}) \cdot \tilde{\mathbf{z}}(-\mathbf{k}) + \left(\frac{N_{Pe}}{N_{Re}} \right) b(\mathbf{k}) b(-\mathbf{k}) \right] \right\} \quad (15)$$

is the analogous functional for convection of a passive additive and implies that the spectral energy and species densities have constant values over wave-number space, with the ratio of Péclet to Reynolds numbers determining the ratio of species to mechanical energy in the spectrum. This extension thus demonstrates equipartition of mechano-chemical energy.

NOTATION

b = independent variable as argument corresponding to concentration in characteristic functional formulation
c = concentration field
c_0 = initial concentration field
$\hat{c}$ = fluctuating component of concentration
$f[\cdot,\cdot]$ = probability density functional
$\mathbf{k}$ = Fourier wave vector
K_{ijk} = projection operator in three-space
$M[\cdot,\cdot]$ = characteristic functional (functional Fourier transform of $f[\cdot,\cdot]$)
N_{Re}, N_{Pe}, N_{Da} = Reynolds, Péclet, Damköhler numbers
T_1^t = semigroup mapping initial velocity field into subsequent velocity fields
$T_{2,\mathbf{u}}^t$ = semigroup mapping initial concentration field into subsequent concentration fields for prescribed velocity field
$\mathbf{u}$ = velocity field
$\mathbf{u}_0$ = initial velocity field
$\mathbf{v}$ = independent variable as argument corresponding to velocity in characteristic functional formulation
$W(\cdot)$ = scalar function satisfying stationary inviscid asymptotic equation
$\mathbf{z}$ = Fourier transform replacing v
$\tilde{\mathbf{z}}$ = Fourier transform, solenoidal
$\underset{\approx}{1}$ = identity operator in three-space
Δ = Laplacian operator in three-space
Δ^{-1} = inverse of Laplacian
∇ = gradient operator in three-space
$\delta/\delta\mathbf{v}$ = functional derivative of first order
$\delta^2/\delta\mathbf{v}^2$ = functional derivative of second order (Laplacian operator in function space $\mathcal{H}^1$)
$\mu_0{}^1(\mathbf{u}_0)$, $\mu^1(\mathbf{u})$ = measures in function spaces of initial and subsequent velocities
$\mu_0{}^2(c_0)$, $\mu^2(c)$ = measures in function spaces of initial and subsequent concentrations
ψ = non-negative function
$\Omega_0{}^1$, $\Omega_0{}^2$ = function spaces of initial velocity and concentration fields
$\mathcal{H}^1$, $\mathcal{H}^2$ = Hilbert spaces of velocity and concentration fields
$[,]$ = scalar products in respective Hilbert spaces

LITERATURE CITED

1. Richardson, L. F., *Proc. Roy. Soc. London,* **110A,** 709 (1926).
2. Batchelor, G. K., "The Theory of Homogeneous Turbulence," Cambridge Univ. Press, England (1960).
3. Batchelor, G. K., and A. A. Townsend, *Proc. Roy. Soc. London,* **194A,** 527 (1948).
4. Lewis, R. M., and R. H. Kraichnan, *Comm. Pure Appl. Math.,* **15,** 397 (1962).
5. Hopf, E., *J. Rational Mech. Anal.,* **1,** 87 (1952).
6. Hopf, E., and E. W. Titt, *J. Rational Mech. Anal.,* **2,** 587 (1953); Hopf, E., *Proc. Symp. Appl. Math.,* **7,** 41 (1957); **12,** 157 (1962).
7. Corrsin, S., *J. Aeronaut. Sci.,* **18,** 417 (1951); *J. Appl. Phys.,* **22,** 469 (1951); *Phys. Fluids,* **1,** 42 (1958) and **7,** 1156 (1964); see also Hinze, J. O., *Turbulence,* McGraw-Hill, New York (1959).
8. Kraichnan, R. H., in S.I. Pai (ed.) "Dynamics of Fluids and Plasmas," Academic Press, New York (1966).

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