

MIXING TO A MOLECULAR LEVEL IN TURBULENT MEDIA

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Abstract—An equation is obtained for the mean product of concentrations of two species in an isotropic stationary random velocity field. The velocity field is assumed to be a normal random process δ -correlated with respect to time. The process of mixing up to a molecular level is shown to be associated with diffusion in the Lagrangian coordinates. The mean species concentration in the Lagrangian variables has been found. The estimates have been made for the rate of growth of the admixture cloud size in the Lagrangian and Eulerian coordinates. The characteristic times of mixing of pre-separated species have been estimated. An expression is obtained for the total product of a slow irreversible second-order chemical reaction at arbitrary initial distributions of reagents. The equilibrium structural function of the passive admixture is given in terms of the structural function of the velocity field.

NOMENCLATURE

b	constant in equation (A3)
$c(x, t)$	concentration at point x and time t
c_1, c_2	concentration of first and second species, respectively
$\langle c_1(Y, t) \rangle_{\mu_1 + \mu_2}$	concentration (averaged over the ensemble of velocity field realizations) of species characterized by the molecular diffusion coefficient equal to $\mu_1 + \mu_2$
$\mathcal{D}(x)$	function defined by equation (21)
$D(x)$	equilibrium structural function of a homogeneous isotropic concentration field
$\mathcal{D}_{LL}(x)$	longitudinal structural velocity function
$\mathcal{D}_{ik}(x)$	function defined by equations (4) and (8)
$\mathcal{G}(x, t), \mathcal{G}(x, t)$	'Lagrangian' Green's function
$G(x, t/y)$	Green's function of equation (7)
k	chemical reaction rate constant
l	inner scale of turbulence
L	outer scale of turbulence
m	exponent in equation (A3)
N	strength of the sources of concentration field fluctuations
$q(x)$	total product of chemical reaction with the initial distribution of reagent concentrations in the form of δ -functions spaced x apart
Q	total product of chemical reaction with arbitrary initial distribution of reagent concentrations
$\overline{r^n}$	Richardson's function moment of order n
$\overline{R^n}$	n -order moment of mean concentration distribution in Lagrangian coordinates
Sc	Schmidt number, ν/μ
t	time
t_i	time required for the width of Lagrangian Green's function to become equal to l

t_m	time of mixing
$v_k(y, t)$	k th Cartesian component of medium velocity at point y and time t
v_L	longitudinal velocity component
Δv_x	characteristic difference between the velocities at two points spaced x apart
x	modulus of vector x , $ x $
x, y	Eulerian position vector
X, Y	Lagrangian position vector
$\overline{X^n}$	n -order moment of Lagrangian Green's function.

Greek symbols

δ	Dirac delta function
$\Gamma(x, t/y)$	Green's function of equation (A2)
Δ	Laplace operator
Δ_x, Δ_y	Laplace operators applied to variables x, y
ε	specific velocity of turbulent energy dissipation
μ	molecular diffusion coefficient
μ_1, μ_2	molecular diffusion coefficient of first and second species, respectively
τ	characteristic time of inner turbulence scale
$\tau(x)$	x -sized vortex lifetime
$\phi(x, t)$	function defined by equation (A1)
$\psi(x, t)$	function defined by equation (6); Richardson's function (34).

Subscripts

i, k	signify the number of Cartesian coordinates which take on the values 1, 2, 3
0	initial value.

Superscripts

0	initial value
.	time derivative
'	spatial derivative.

1. INTRODUCTION

THE MIXING of reagents up to a molecular level is an important aspect of the problem of chemical reactions in turbulent media [1]. The molecular-level mixing at a certain point in space means that at this point the concentrations of all the substances being mixed become simultaneously different from zero. The rate of mixing governs the yield of the chemical reaction product. In particular, the rate of substance formation in a very fast chemical reaction is limited by the finite rate of mixing.

It has long been known that the rate of mixing in turbulent media is much faster than in laminar ones. The first estimates of the mixing rate were made by Corrsin [2-4] who estimated the time for the decay of fluctuations of a statistically homogeneous concentration field. It is the disappearance of fluctuations which indicates that the added material has been mixed up to the molecular level with the host medium. In a typical case of moderate Schmidt numbers this time has turned to be equal to the lifetime of a vortex having the size of the order of the outer scale of the concentration field.

In recent times a number of problems of chemical reactions have been considered and in this way the problem of mixing has also been touched to some extent. By using different closure methods for the moment equations, one- and two-component second-order reactions have been studied in detail at the final stage of turbulence decay when the medium motion can be neglected [5-7]. It was shown in refs. [7-9] that the problem of a very fast two-component second-order reaction is reduced to the problem of finding the one-point distribution function of the substance concentration in the absence of a chemical reaction. A detailed discussion of the methods used for the purpose is given elsewhere [10]. Some aspects of chemical reactions involving heat generation were considered in ref. [11].

The present paper concerns itself with the problem of mixing of pre-separated species up to the molecular level in the absence of chemical reactions. This paper differs from the other reported studies in the method of solution and in a more general statement of the problem which is formulated as follows.

Suppose that at the initial instant of time the arbitrary distributions of concentrations $c_1^0(\mathbf{x})$ and $c_2^0(\mathbf{x})$ of two species with unit masses are assigned in the turbulent medium. The statistical characteristics of the velocity field are assumed to be given and independent of the above species in the medium, while the coefficients of molecular diffusion of species are assumed to be independent of their concentrations. The random velocity-averaged product of concentrations $\langle c_1(\mathbf{x}, t) c_2(\mathbf{x}, t) \rangle$ at any subsequent time is required. This product may serve as a quantitative characteristic of the extent of mixing of species up to the molecular level. Just as in all the previous works dealing with this subject, the derivation of the basic equations in this work is based on some simplifying assumptions the main one being the assumption that the velocity field is

δ -correlated in time. In order to check the validity of the initial equations obtained in this way, they were used for solving a number of 'test' problems of turbulent mixing. Thus, without resorting to any additional arguments following, for example, from the dimensional or similarity theories, the Richardson 4/3rd law has been obtained as well as the equilibrium structural function of the isotropic concentration field pointing to the fact that the approximation used for the problem of turbulent mixing is quite reasonable.

2. BASIC EQUATIONS

Let us derive an equation which would govern a more general object of investigation $\langle c_1(\mathbf{y}, t) c_2(\mathbf{y} + \mathbf{x}, t) \rangle$. The starting equations will be the dynamic equations for concentration in a moving medium. In particular, the equation for the concentration of the first species is

$$\frac{\partial c_1(\mathbf{y}, t)}{\partial t} + v_k(\mathbf{y}, t) \frac{\partial c_1(\mathbf{y}, t)}{\partial y_k} = \mu_1 \Delta c_1(\mathbf{y}, t), \quad (1)$$

where $v_k(\mathbf{y}, t)$ is the k th component of the incompressible liquid velocity at the point \mathbf{y} at time t ; and μ_1 is the coefficient of the molecular diffusion of the first species. The equation for $c_2(\mathbf{y} + \mathbf{x}, t)$ has a similar form. Multiplying equation (1) by $c_2(\mathbf{y} + \mathbf{x}, t)$, and the equation for the concentration of the second substance by $c_1(\mathbf{y}, t)$, and then adding them together, we shall obtain, after averaging over a random velocity field, the following equation

$$\begin{aligned} & \left[\frac{\partial}{\partial t} - \mu_1 \left(\frac{\partial}{\partial y_k} - \frac{\partial}{\partial x_k} \right)^2 - \mu_2 \frac{\partial^2}{\partial x_k^2} \right] \\ & \times \langle c_1(\mathbf{y}, t) c_2(\mathbf{y} + \mathbf{x}, t) \rangle + \left(\frac{\partial}{\partial y_k} - \frac{\partial}{\partial x_k} \right) \\ & \times \langle v_k(\mathbf{y}, t) c_1(\mathbf{y}, t) c_2(\mathbf{y} + \mathbf{x}, t) \rangle + \frac{\partial}{\partial x_k} \\ & \times \langle v_k(\mathbf{y} + \mathbf{x}, t) c_1(\mathbf{y}, t) c_2(\mathbf{y} + \mathbf{x}, t) \rangle = 0. \end{aligned} \quad (2)$$

In order to calculate the mean product of the velocity and concentrations, being the functional of the velocity, we suppose that the velocity is the Gaussian random process δ -correlated in time. By applying the method suggested in ref. [12], a detailed description of which is given in refs. [13, 14], we obtain for the case of the stationary isotropic velocity field:

$$\begin{aligned} & \langle v_k(\mathbf{z}, t) c_1(\mathbf{y}, t) c_2(\mathbf{y} + \mathbf{x}, t) \rangle \\ & = - \left[B_{kj}(\mathbf{z} - \mathbf{y}) \left(\frac{\partial}{\partial y_j} - \frac{\partial}{\partial x_j} \right) + B_{kj}(\mathbf{z} - \mathbf{y} - \mathbf{x}) \frac{\partial}{\partial x_j} \right] \\ & \quad \times \langle c_1(\mathbf{y}, t) c_2(\mathbf{y} + \mathbf{x}, t) \rangle, \end{aligned} \quad (3)$$

where

$$B_{kj}(\mathbf{z} - \mathbf{y}) = \int_{-\infty}^t \langle v_k(\mathbf{z}, t) v_j(\mathbf{y}, t') \rangle dt'. \quad (4)$$

By substituting equation (3) into equation (2) and taking into account the incompressibility, we obtain

the following equation for the mean product of concentrations

$$\begin{aligned} & \left[\frac{\partial}{\partial t} - B_{kj}(0) \left(\frac{\partial^2}{\partial y_k \partial y_j} - 2 \frac{\partial^2}{\partial y_k \partial x_j} \right) \right. \\ & \quad \left. + 2 \frac{\partial^2}{\partial x_k \partial x_j} \right] + 2B_{kj}(x) \left(\frac{\partial^2}{\partial x_k \partial x_j} - \frac{\partial^2}{\partial y_k \partial x_j} \right) \\ & \quad - \mu_1 \left(\Delta_x + \Delta_y - 2 \frac{\partial^2}{\partial x_k \partial y_k} \right) - \mu_2 \Delta_x \Big] \\ & \quad \times \langle c_1(y, t) c_2(y + x, t) \rangle = 0. \end{aligned} \quad (5)$$

Henceforth, we will be interested in the volume-integral product of concentrations

$$\psi(x, t) = \int \langle c_1(y, t) c_2(y + x, t) \rangle dy. \quad (6)$$

The equation for $\psi(x, t)$ is obtained by integration of equation (5) over y :

$$\frac{\partial \psi}{\partial t} = \mathcal{D}_{ik}(x) \frac{\partial^2 \psi}{\partial x_i \partial x_k} + (\mu_1 + \mu_2) \Delta \psi, \quad (7)$$

in which

$$\mathcal{D}_{ik}(x) = 2[B_{ik}(0) - B_{ik}(x)]. \quad (8)$$

3. DIFFUSION IN THE LAGRANGIAN COORDINATE SYSTEM AND MIXING

One of the main outcomes of this study is a constructive description of mixing and diffusion of admixtures in the Lagrangian system of coordinates. As is known, the Lagrange approach is based on the study of the behaviour of fluid particles tagged by one or another means. The natural label is usually taken to be the Eulerian coordinate of a fluid particle at the initial instant of time [15]. In principle, the Euler and Lagrange approaches are equivalent, and a choice between the two may be made only on the basis of the nature of the problem studied.

An attractive feature of the Lagrangian description of mixing is the fact that at the zero coefficient of molecular diffusion the concentration of the passive admixture is not altered during the motion of a fluid particle and thus is independent of the random velocity field. This is easily seen from equation (1), which at $\mu = 0$ takes on the form

$$\frac{D}{Dt} c(y, t) = 0, \quad (9)$$

where D/Dt is the operator giving the material derivative. It follows from the above equation that at $\mu = 0$ the concentration of the passive admixture retains its initial value in the Lagrangian variables.

The process of mixing within the entire volume is characterized by the quantity

$$\psi(0, t) = \int \langle c_1(y, t) c_2(y, t) \rangle dy. \quad (10)$$

Converting in equation (10) to the Lagrangian coordinate system Y and taking into account that for the incompressible liquid the transformation Jacobian between the Euler and Lagrange coordinates is equal to unity [15], we obtain

$$\begin{aligned} \psi(0, t) &= \int \langle c_1[y(Y, t), t] c_2[y(Y, t), t] \rangle dY \\ &= \int \langle c_1(Y, t) c_2(Y, t) \rangle dY. \end{aligned} \quad (11)$$

The use of the hypothesis concerning the δ -correlationability of velocity field allows one to realize the consequences of equation (9) in a simple analytical form. As it follows from equation (7), the function $\psi(x, t)$ depends only on the sum of the molecular diffusion coefficients. Therefore, the result of mixing equation (11) will remain the same if we assume that one of the species, e.g. the second one, has a zero diffusion coefficient, while the first has the diffusion coefficient which is equal to $\mu_1 + \mu_2$. Taking into account the above invariance of concentration distributions in the Lagrangian variables at zero diffusion coefficients, we may write

$$\begin{aligned} \psi(0, t) &= \int \langle c_1(Y, t) |_{\mu_1 + \mu_2} \cdot c_2(Y, t) |_{\mu = 0} \rangle dY \\ &= \int \langle c_1(Y, t) |_{\mu_1 + \mu_2} \rangle c_2^0(Y) dY. \end{aligned} \quad (12)$$

On the other hand, equation (7) yields

$$\psi(0, t) = \int G(0, t/y) \psi(y, 0) dy, \quad (13)$$

where $G(x, t/y)$ is the Green's function of equation (7) which corresponds to the initial δ -function at the point y . Taking into consideration the symmetry of the Green's function over the spatial variables, which follows from the Hermitian nature of the spatial part of the operator in equation (7), and the definition (6) of the function ψ , we obtain

$$\begin{aligned} \psi(0, t) &= \int G(y, t/0) c_1^0(z) c_2^0(z + y) dz dy \\ &= \int G(y_2 - y_1, t/0) c_1^0(y_1) c_2^0(y_2) dy_1 dy_2. \end{aligned} \quad (14)$$

Integration in equation (14) can be considered to be performed over the position of fluid particles at the initial time instant, i.e. actually over the Lagrangian variables. Therefore, equation (14) can be rewritten in the form

$$\psi(0, t) = \int G(Y_2 - Y_1, t/0) c_1^0(Y_1) c_2^0(Y_2) dY_1 dY_2. \quad (15)$$

Setting equation (12) equal to equation (15) and taking into account the arbitrariness of the initial distribution of c_2^0 , gives the expression for the mean concentration of the species, the molecular diffusion coefficient of which is equal to $2\mu = \mu_1 + \mu_2$, in the

Lagrangian coordinates

$$\langle c(\mathbf{X}, t) \rangle = \int \mathcal{G}(\mathbf{X} - \mathbf{Y}, t) c^0(\mathbf{Y}) d\mathbf{Y}, \quad (16)$$

where $\mathcal{G}(\mathbf{X}, t) = G(\mathbf{X}, t/0)$ is the so-called Lagrangian Green's function. It describes the mean concentration of the species at time t at the Lagrangian point \mathbf{X} under the condition that at $t = 0$ it was concentrated at $\mathbf{X} = 0$. In the case of an isotropic velocity field, the Lagrangian Green's function depends only on the absolute value of the argument

$$\mathcal{G}(\mathbf{X}, t) = \mathcal{G}(X, t), \quad (17)$$

and satisfies the equation

$$\dot{\mathcal{G}}(x, t) = x^{-2} \{x^2 [2\mu + \mathcal{D}(x)] \mathcal{G}'(x, t)\}', \quad (18)$$

subject to the initial condition

$$\mathcal{G}(x, 0) = -\frac{1}{2\pi} \frac{\delta'(x)}{x}, \quad (19)$$

where

$$\mathcal{D}(x) = \int_{-\infty}^t \langle [v_L(0, t) - v_L(x, t)] \times [v_L(0, t') - v_L(x, t')] \rangle dt', \quad (20)$$

and v_L is the velocity component parallel to x . Equation (18) is obtainable from equation (7) if the spherical symmetry of the solution, the isotropic nature of the tensor \mathcal{D}_{ik} and fluid incompressibility, are taken into account.

The analytical form of the function $\mathcal{D}(x)$, having the meaning of the 'turbulent' diffusion coefficient, is unknown within the entire region of the argument variation. This prevents the analytical solution of equation (18) being valid for all the values of x . The function $\mathcal{D}(x)$ can be estimated by the formula $\mathcal{D}(x) \sim \mathcal{D}_{LL}(x) \cdot \tau(x)$, where $\mathcal{D}_{LL}(x)$ is the longitudinal structural velocity function, and $\tau(x)$ is the lifetime of the x -sized vortex determined by the difference of velocities $\Delta v_x \sim \sqrt{[\mathcal{D}_{LL}(x)]}$ at the distance x : $\tau(x) \sim x/\Delta v_x$. As a result we obtain

$$\mathcal{D}(x) \sim \begin{cases} v \left(\frac{x}{l}\right)^2, & x \ll l, \\ \varepsilon^{1/3} x^{4/3} \sim v \left(\frac{x}{l}\right)^{4/3}, & l \ll x \ll L, \\ \varepsilon^{1/3} L^{4/3}, & x \gg L, \end{cases} \quad (21a)$$

$$(21b)$$

$$(21c)$$

where l and L is the inner and outer turbulence scale, respectively; ε is the specific rate of turbulent energy dissipation; and v the molecular viscosity of the medium.

Equation (18) was investigated for each of the functions $\mathcal{D}(x)$ in equations (21). The analytical solution of equation (18) obtained for the scales less than l , where $\mathcal{D} \sim x^2$, is given elsewhere [20]. The solution of equation (18) at $\mu = 0$ involving the function $\mathcal{D}(x)$, given by relation (21b), is presented in the Appendix for the inertia range of scales. A more

complete investigation of equation (18), using the experimental data to determine $\mathcal{D}(x)$ within the entire range of the values of x , appears to be feasible only by numerical methods. However, the basic qualitative principles of diffusion (in the Lagrange coordinates) and of mixing can be established by not resorting to the solution of equation (18) but rather restricting ourselves only to the study of the moments of the Lagrangian Green's function.

4. THE LAGRANGIAN SIZE OF THE ADMIXTURE CLOUD AND THE TIME OF MIXING

The results obtained in Section 3, in particular equation (12), allow the interpretation of the process of mixing of two species as the 'spreading', in the Lagrangian coordinate system, of the cloud of one of the species diffusing with the total diffusion coefficient, over the initial distribution of concentration of the other species. The mixing of the pre-separated species will occur after a noticeable overlapping of these distributions. This requires a corresponding increase in the size of the admixture cloud in the Lagrangian coordinate system. The mixing time is understood to be a period during which this overlapping will occur. It is apparent that in order to determine the mixing time it is necessary to know the time dependence of the Lagrangian size of the admixture cloud. The Lagrangian size of the diffusing admixture cloud at time t has a simple geometrical meaning: this is the initial (at $t = 0$) distance between the fluid particles into which the admixture has diffused by the time t .

In an isotropic turbulent medium the position of the admixture cloud centroid in both the Eulerian and Lagrangian coordinates does not depend on time. By matching the coordinate origin with the cloud centroid we will obtain, with account for equation (16), the following expression for the RMS size of the admixture cloud in the Lagrangian coordinates

$$\begin{aligned} \overline{R^2(t)} &= \int X^2 \langle c(\mathbf{X}, t) \rangle d\mathbf{X} \\ &= \int X^2 \mathcal{G}(\mathbf{X} - \mathbf{Y}, t) c^0(\mathbf{Y}) d\mathbf{Y} d\mathbf{X}. \end{aligned} \quad (22)$$

Employing the substitution $\mathbf{Z} = \mathbf{X} - \mathbf{Y}$ in the above equation and taking into consideration that because of the parity of the Lagrangian Green's function its first moment is equal to zero, we obtain

$$\overline{R^2(t)} = \overline{R_0^2} + \overline{X^2(t)}, \quad (23)$$

where $\overline{R_0^2}$ is the mean square of the initial cloud size; $\overline{X^2(t)}$ is the mean square of the width of the Lagrangian Green's function which describes the admixture cloud with the initial concentration distribution in the form of the δ -function

$$\overline{X^2(t)} = 4\pi \int_0^\infty X^4 \mathcal{G}(X, t) dX. \quad (24)$$

It follows from equation (23) that the Lagrangian RMS size of the cloud is equal to its initial value summed up with the mean square of the Lagrangian Green's function width. For short times, when this width is much less than l , relations (18) and (21a) yield equation (24) for the Lagrangian size the solution of which, with equation (19) taken into account, is

$$\overline{X^2(t)} = 12\mu\tau \left(\exp \frac{t}{\tau} - 1 \right), \quad (25)$$

where τ is the characteristic time of the inner turbulence scale

$$\tau = 0.1 l^2/\nu. \quad (26)$$

Equation (25) is valid for the times not exceeding the time

$$t_l = \tau \ln \left(1 + \frac{5}{6} \frac{\nu}{\mu} \right), \quad (27)$$

during which the Lagrangian size attains the value $\sim l$.

It follows from equation (25) that the initial (at $t \lesssim \tau$) expansion of the cloud occurs at the expense of molecular diffusion without the interaction with hydrodynamics. For the species, for which $\mu \sim \nu$, the role of hydrodynamics is relatively insignificant over the whole stage of cloud expansion up to the size $\sim l$, which is attained for the time $\sim \tau$. For the species for which $\mu \ll \nu$, at the times within the range $\tau < t < t_l$, the Lagrangian size increases exponentially which is due to the exponential growth in time of the mean concentration gradients occurring on the scales smaller than l [16]. Note that according to equations (23) and (25) at $\mu = 0$ the Lagrangian size of the cloud does not increase. This means that the admixture remains within the same fluid particles into which it penetrated initially. In other words, as time proceeds, at $\mu = 0$, the fluid particles, different from those which were coloured in the beginning, retain their initial colour. Yet, the increase of the Lagrangian size of the cloud may occur only as a result of the appearance of additional 'coloured' particles. Consequently, it is impossible to mix the preprepared species having $\mu_1 = \mu_2 = 0$ up to the molecular level.

In order to estimate the size of the region where the Lagrangian Green's function is noticeably different from zero, there is no need to solve equation (18). Express $\mathcal{G}(x, t)$ from equation (18) in terms of $\mathcal{G}(x, t)$ and integrate the result with respect to time from 0 to t

$$\int_0^t \mathcal{G}(x, t) dt = \int_x^\infty \frac{dy}{y^2 [2\mu + \mathcal{D}(y)]} \times \int_y^\infty [\mathcal{G}(z, t) - \mathcal{G}(z, 0)] z^2 dz. \quad (28)$$

By substituting the initial condition (19) into equation (28) and integrating both sides of equation (28) over the volume, we obtain

$$3t = \int_0^\infty 4\pi x^2 \mathcal{G}(x, t) dx \int_0^x \frac{y dy}{2\mu + \mathcal{D}(y)}. \quad (29)$$

This relation can be used to estimate the Lagrangian size of the cloud for the times that exceed t_l . When the cloud size lies within the inertia interval, then the main contribution to the integral (29) comes from the values of x within this interval. For such values of the upper limit, the internal integral in equation (29) can be evaluated using relations (21a) and (21b). At $x \gg l$, for the typical case of $\mu \sim \nu$ the value of the internal integral is equal to $\sim \varepsilon^{-1/3} x^{2/3}$, which, after substitution into equation (29), gives

$$\int_0^\infty 4\pi x^2 \mathcal{G}(x, t) x^{2/3} dx \equiv \overline{X^{2/3}(t)} \sim \varepsilon^{1/3} t. \quad (30)$$

Thus, if the Lagrangian sizes of the cloud fall within the inertia scale interval, the 2/3rd moment of mean concentration distribution increases linearly with time.

If the cloud, originating from the initial δ -function, has expanded in the Lagrangian coordinates up to the dimensions that substantially exceed L , then, as follows from equations (21) and (29), the law which governs its expansion at times exceeding the time of attainment of the size $\sim L$, is of the form

$$\overline{X^2(t)} \sim 6\varepsilon^{1/3} L^{4/3} t. \quad (31)$$

The mixing time t_m depends on the initial concentration distributions. Let, for the sake of definiteness, the first species be concentrated within the volume having the characteristic size R_0 , while the second be distributed in the space outside this volume. In this case, the time t_m , according to equation (12), is, by the order of magnitude, the time of doubling the Lagrangian volume of the first species, or, as it follows from equation (23), is equal to the time during which the size of the Lagrangian Green's function will become comparable with the initial size of the admixture cloud:

$$\overline{X^2(t_m)} = R_0^2. \quad (32)$$

It is easily seen that the above equality can be also applied to estimate the time of mixing of two species which initially occupied the volumes of the size $\sim R_0$, spaced by the distance $\sim R_0$, and of the species the initial concentration distributions of which had the form of the δ -functions spaced by the distance R_0 . For these types of initial distributions the mixing time estimated by equation (32) with equations (25), (30) and (31) taken into account, is equal, by order of magnitude, to

$$t_m \sim \tau \ln \left[1 + \frac{5}{3} \frac{\nu}{\mu_1 + \mu_2} \left(\frac{R_0}{l} \right)^2 \right], \quad R_0 \ll l, \quad (33a)$$

$$t_m \sim \begin{cases} R_0^{2/3} \varepsilon^{-1/3}, & l \ll R_0 \ll L, \\ R_0^2 \varepsilon^{-1/3} L^{-4/3}, & R_0 \gg L, \end{cases} \quad (33b)$$

$$t_m \sim \begin{cases} R_0^{2/3} \varepsilon^{-1/3}, & l \ll R_0 \ll L, \\ R_0^2 \varepsilon^{-1/3} L^{-4/3}, & R_0 \gg L, \end{cases} \quad (33c)$$

Expressions (33b) and (33c) are valid for $Sc \sim 1$.

The estimation of the damping time for a statistically uniform field of concentrations having the outer scale within the inertia interval has been made elsewhere [4]. For the numbers $Sc \sim 1$ this estimate coincides with that given by equation (33b).

5. THE EULERIAN SIZE OF THE CLOUD

Setting $c_1 = c_2 = c(y, t)$ in equation (6), we obtain that the quantity $\psi(x, t)$ transforms into the Richardson function [16]

$$\psi(x, t) = \int \langle c(y, t) c(y + x, t) \rangle dy, \quad (34)$$

with the help of which it is possible to determine the mean Eulerian size of the cloud of a diffusing admixture [with the distribution of concentration $c(y, t)$] in a coordinate system with its origin located at the cloud centroid. In an isotropic turbulence, at a spherically symmetrical initial distribution of concentration, the Richardson function is spherically symmetrical and obeys the equation the form of which coincides with equation (18)

$$\dot{\psi}(x, t) = x^{-2} \{x^2 [2\mu + \mathcal{D}(x)] \psi'(x, t)\}', \quad (35)$$

where μ is the coefficient of molecular diffusion of the species considered.

When the initial concentration distribution has the form of the δ -function, the initial Richardson function is determined by equation (19). In this case the Richardson function coincides with the Lagrangian Green's function, and for the Eulerian dimensions of the cloud characterized by the moments

$$\overline{r^n(t)} \equiv \int_0^\infty 4\pi x^{n+2} \psi(x, t) dx, \quad (36)$$

the estimates given by equations (25), (30) and (31) are valid.

It is not difficult to estimate the size of the cloud also in the case of an arbitrary, initial, spherically symmetrical distribution of concentration. When the size of the cloud is much less than l , then equations (35) and (21a) may yield the equation for the second moment from equation (36), the solution of which is

$$\overline{r^2(t)} = \overline{r_0^2} \exp \frac{t}{\tau} + 12\mu\tau \left(\exp \frac{t}{\tau} - 1 \right), \quad (37)$$

where $\overline{r_0^2}$ is the second moment of the initial Richardson function.

It follows from equation (37) that for the time $t \sim \tau$ the size of the cloud increases at the expense of molecular diffusion and convective transport of the substance, the contributions of which are proportional to $12\mu\tau$ and $\overline{r_0^2}$. If $\mu \sim v$, then by the time $t \sim \tau$ the cloud will have attained the size $\sim l$ and its further increase cannot be described by equation (37). If $\mu \ll v$, then by the time $t \sim \tau$ the size of the cloud will have become much smaller and its subsequent expansion up to the size $\sim l$ will have an exponential character. This is due to an exponentially rapid increase of the mean distance between the fluid particles on the scales $\sim l$ [16]. Note that if the initial size of the cloud differs from zero, the Eulerian size, in contrast to the Lagrangian one, increases also at $\mu = 0$.

When the size of the diffusing admixture cloud

exceeds the inner scale l , then the size of the cloud can be estimated with the aid of the relationship similar to equation (29), namely

$$3t = \int_0^\infty 4\pi [\psi(x, t) - \psi(x, 0)] x^2 dx \int_0^x \frac{y dy}{2\mu + \mathcal{D}(y)}, \quad (38)$$

which is derived from equation (35) provided $\psi(x, t)$ is replaced by $\dot{\psi}(x, t)$ and the expression obtained for $\dot{\psi}$ is integrated over the whole space with respect to time from 0 to t .

Applying the reasoning similar to that used for the derivation of equations (30) and (31), we obtain from equation (38)

$$\overline{r^{2/3}(t)} = \overline{r_0^{2/3}} + \varepsilon^{1/3} t \quad (l \ll r_0, r \ll L), \quad (39)$$

$$\overline{r^2(t)} = \overline{r_0^2} + 6\varepsilon^{1/3} L^{4/3} t \quad (r_0 \gg L). \quad (40)$$

Equation (39) is one of the forms of representation of the Richardson 4/3rd law [16].

By comparing equations (37), (39) and (40) with equations (33) we may conclude that in the process of turbulent diffusion at $\mu \sim v$ a considerable portion of the cloud mixes with the surrounding medium up to the molecular level for the time during which the Eulerian size of the cloud doubles. Moreover, it follows from equations (30), (31), (39) and (40) that at $\mu \sim v$ the Lagrangian size of the cloud coincides with the Eulerian one, if these are much larger than the initial size and the inner scale l .

6. THE TOTAL PRODUCT OF CHEMICAL REACTION

The results obtained in this work can be applied to the study of fairly slow chemical reactions in which the concentration of reacting components is determined mainly by mixing and is virtually independent of the reaction rate. As an example having relevance to the process occurring in the atmosphere and the ocean, consider a reaction in an infinite space between the species initially concentrated in limited volumes. In contrast to the case of very fast reactions, in which the rate of the final product yield increases with turbulence intensity, in the example considered the enhancement of turbulence decreases the final product yield. This is explained by acceleration of the turbulent diffusion process which scatters the species *ad infinitum* well before they have time to react.

Let the first and second species form, while mixing, the third substance as a result of the irreversible second-order chemical reaction. The reaction rate is independent of temperature and is so slow that a reaction-produced change in the substance concentration can be neglected. In this case the quantity of the third substance Q , produced within the whole volume for the time from 0 to ∞ (the total product of the chemical reaction) is proportional to the time integral of equation (12) and, with equations (16) and (17) taken

into consideration can be given as

$$Q = \int q(|x-y|)c_1^0(x)c_2^0(y) dx dy, \quad (41)$$

where

$$q(x) = k \int_0^\infty \mathcal{G}(x, t) dt, \quad (42)$$

and k is the chemical reaction rate constant.

The function $q(x)$ has the meaning of the total product of the reaction at the initial concentrations in the form of δ -functions spaced by the distance x .

In order to determine $q(x)$, we shall use equation (28). By virtue of equation (19), the term in equation (28), which contains the initial value of $\mathcal{G}(z, 0)$, becomes zero. In addition, for rather long times, the 'width' of the function $\mathcal{G}(z, t)$ at $\mu \neq 0$ is so large that at the final values of y , which contribute mainly to equation (28)

$$4\pi \int_y^\infty \mathcal{G}(z, t) z^2 dz \rightarrow 1 \quad \text{at } t \rightarrow \infty. \quad (43)$$

Therefore

$$q(x) = \frac{k}{4\pi} \int_x^\infty \frac{dy}{y^2 [\mu_1 + \mu_2 + \mathcal{D}(y)]}. \quad (44)$$

It follows from equation (44) that with a decreasing distance x between the δ -functions, the total chemical reaction product increases. This is attributed to the fact that with a decrease in x the characteristic values of concentrations in the clouds increase at the stage of their substantial overlapping. Moreover, it can also be seen from equation (44) that with the growth of the turbulence intensity [at higher $\mathcal{D}(y)$] the chemical product yield decreases. This can be explained by an increase in the rate of cloud spreading which reduces the time of contact of the components.

7. THE EQUILIBRIUM STRUCTURAL FUNCTION OF THE CONCENTRATION FIELD

Let us direct our attention to the initial equation (5) in which c_1 and c_2 are now understood to represent the concentration of the same species and let us assume that the concentration field is uniform and isotropic. In this case equation (5) goes over into the equation for the correlational (structural) function of concentration the form of which coincides with equation (18). By introducing into equation (18), similar to refs. [17, 18], the source of fluctuations with the power N , required for the stationary regime to be realized, we obtain the equilibrium structural concentration function

$$D(x) = \frac{4N}{3} \int_0^x \frac{y dy}{2\mu + \mathcal{D}(y)}. \quad (45)$$

Within the limit $x \rightarrow 0$, $D(x) \sim (N/3\mu)x^2$, while over the inertia interval $D(x) \sim 2N\epsilon^{-1/3}x^{2/3}$. This agrees with the results obtained in refs. [17, 18].

8. CONCLUSION

The paper considered the processes of mixing and diffusion in random velocity field. The main assumption, which allowed the splitting of the velocity correlation and the concentration product and the derivation of the basic equations (5) and (7), is the assumption that the velocity field is the Gaussian process δ -correlated with respect to time. It is known that the approximation of this velocity field poorly applies to the description of the turbulent motion of fluid particles in a fixed coordinate system [13]. However, this approximation, when used to describe the phenomena based on the relative motion of fluid particles, leads to physically reasonable results. Thus, it shows an exponential growth in time of the mean distance between the fluid particles on the inner scale of turbulence [13]. It has been shown in the present work that the approximation to the Richardson 4/3rd law, to the structural function of concentration field with correct asymptotic behaviour, to the conclusion on the impossibility of mixing the substances which have zero coefficients of molecular diffusion. The above allows one to hope that the application of the Gaussian δ -correlated process to the description of mixing of different substances and of their diffusion in the Lagrangian coordinates will also lead to physically reasonable results. Note that the accurate results (41) and (44) which follow from the mixing theory developed and which have a bearing on the total chemical reaction product can be relatively easily checked by experiment.

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APPENDIX

Assuming $\mu = 0$ in equations (18) and (35) and introducing the notation

$$\psi(x, t) = x^{-1}\phi(x, t), \quad (\text{A1})$$

we obtain for $\phi(x, t)$ the following equation

$$\dot{\phi} = \mathcal{D}\phi'' + \mathcal{D}'\phi' - x^{-1}\mathcal{D}'\phi. \quad (\text{A2})$$

Let us represent $\mathcal{D}(x)$ in a more general, than in equation (18b), form

$$\mathcal{D}(x) = bx^m, \quad (0 \leq m < 2), \quad (\text{A3})$$

where b is a constant.

Solving equation (A2), with account for equation (A3), by the method of separation of variables and using the Hankel transformation [19], we find the Green's function, equation (A2), corresponding to the initial δ -function at the point y

$$\Gamma(x, t/y) = \frac{(xy)^{(1-m)/2}}{(2-m)bt} \exp \left[-\frac{x^{2-m} + y^{2-m}}{(2-m)bt} \right] \times I_{(m+1)/(2-m)} \left[2 \frac{(xy)^{(2-m)/2}}{bt(2-m)^2} \right], \quad (\text{A4})$$

where I is the modified Bessel function.

Equation (31) at $\mu = 0$ goes over into the equation for the probability density of the distance x between a pair of fluid particles in isotropic turbulence [13]. Therefore, the solution (A4) makes it possible to write out the probability for detecting the fluid particles at time t and distance x if at $t = 0$ they were at the distance x_0 :

$$4\pi x^2 \psi(x, t) = \frac{x}{x_0} \Gamma(x, t/x_0). \quad (\text{A5})$$

The transition probability (A5) at $m = 4/3$ can be used for the analysis of cloud expansion in the inertia interval of scales.

MELANGE A L'ECHELLE MOLECULAIRE DANS UN MILIEU TURBULENT

Résumé—On obtient une équation pour les concentrations moyennes de deux espèces dans un champ de vitesses aléatoires isotrope en moyenne. Le champ des vitesses est supposé être un processus aléatoire normal δ -corrélé par rapport au temps. Le mécanisme de mélange à l'échelle moléculaire est associé à la diffusion dans les coordonnées lagrangiennes. La concentration moyennes des espèces est donnée; l'estimation est faite pour la croissance de la taille du nuage dans les coordonnées lagrangienne et eulerienne. Les temps caractéristiques de mélange des espèces sont estimés. On obtient une expression pour le produit global d'une réaction chimique irréversible de second ordre, avec des distributions initiales arbitraires de réactants. La fonction structurelle d'équilibre de mélange passif est donnée à partir de la fonction structurelle du champ de vitesse.

MISCHEN BIS ZUM MOLEKULAREN BEREICH IN EINEM TURBULENTEN MEDIUM

Zusammenfassung—Für die mittleren Konzentrationen zweier Stoffe in einem isotropen stationären ungerichteten Geschwindigkeitsfeld wird eine Gleichung angegeben. Es wird angenommen, daß das Geschwindigkeitsfeld eine normale Zufallsverteilung mit δ -Korrelation bezüglich der Zeit hat. Es zeigt sich, daß der Vorgang der Mischung bis in den molekularen Bereich mit der Diffusion in Lagrangeschen Koordinaten verknüpft ist. Die mittlere Teilchenkonzentration in Lagrangeschen Variablen wurde gefunden. Die Berechnungen wurden für die Ausbreitungsgeschwindigkeit der Zumischwolke in Lagrangeschen und Eulerschen Koordinaten gemacht. Die charakteristischen Mischzeiten von vorsortierten Stoffen wurden berechnet. Ein Ausdruck für das Endprodukt einer langsamen irreversiblen chemischen Reaktion zweiter Ordnung bei vorgegebener Anfangsverteilung der Reaktionspartner wurde erhalten. Die strukturelle Gleichgewichtsfunktion des passiven Zumischstoffes wird in Abhängigkeit von der strukturellen Funktion des Geschwindigkeitsfeldes angegeben.

СМЕШЕНИЕ ДО МОЛЕКУЛЯРНОГО УРОВНЯ В ТУРБУЛЕНТНЫХ СРЕДАХ

Аннотация—Получено уравнение для среднего произведения концентраций двух веществ в изотропном стационарном случайном поле скоростей. Предполагается, что поле скоростей есть нормальный, δ -коррелированный по времени случайный процесс. Показано, что процесс смешения до молекулярного уровня связан с диффузией в лагранжевых координатах. Найдена средняя концентрация вещества в лагранжевых переменных. Сделаны оценки скорости роста размеров облака примеси в лагранжевых и эйлеровых координатах. Оценены характерные времена смешения предварительно разделенных веществ. Получено выражение для суммарного продукта медленной необратимой химической реакции второго порядка при произвольных начальных распределениях реагентов. Равновесная структурная функция пассивной примеси выражена через структурную функцию поля скоростей.