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A Model of Turbulent Mixing in the $A + B \rightarrow 0$ Reaction

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The diffusion limited reaction $A + B \rightarrow 0$ in sufficiently low dimensions results in macroscopically self-regregated systems with anomalous reaction rate laws. When the chemical mixture is embedded in a fluctuating velocity field having statistics mimicking "turbulent diffusion" the effects of spatial inhomogeneities are washed out and the classical global reaction rate laws in three dimensions result.

KEY WORDS: $A + B \rightarrow 0$; turbulent mixing.

1. INTRODUCTION

It has been over a decade since Zeldovich and co-workers$^{(1)}$ pointed out that the diffusion-limited reaction $A + B \rightarrow 0$ in sufficiently low dimensions will result in macroscopically self-segregated systems with anomalous reaction rate laws. Since that time there has been an explosion of interest in this phenomenon, the vast majority of studies focusing on various microscopic mechanisms that might modify the originally deduced behavior, e.g., the effects of traps,$^{(2)}$ desorption (e.g., ref. 3), various reaction laws,$^{(4)}$ etc. On the other hand, there has been little or no attention paid to the possible modification of these predictions due to such effects as stirring or shaking the chemical mixture to create a turbulent flow field in which the reaction takes place. Herein we study the effect of a simple model of a fluctuating velocity field on the reaction rate law for the $A + B \rightarrow 0$ reaction.

Let us briefly review how one traditionally characterizes the behavior of the class of $A + B \rightarrow 0$ reactions by means of rate laws. If $\rho_i(\mathbf{r}, t)$,

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$i = \mathrm{A, B}$, is the position-dependent particle density, then in a volume V one constructs rate laws for the averaged quantity

$$\rho_i(t) \equiv \frac{1}{V}\int_V d\mathbf{r}\, \rho_i(\mathbf{r}, t), \qquad i = \mathrm{A, B} \tag{1.1}$$

such that

$$\frac{d\rho_i}{dt}(t) = F\{\rho_{\mathrm{A}}, \rho_{\mathrm{B}}\} \tag{1.2}$$

in the absence of time- and/or space-dependent sources. Thus, for the $\mathrm{A} + \mathrm{B} \to 0$ reaction the textbook global rate laws are

$$\dot{\rho}_i(t) = -k_g \rho_{\mathrm{A}}(t)\, \rho_{\mathrm{B}}(t) + R_{ig}(t) \tag{1.3}$$

where k_g is the global rate coefficient that is independent of time and of system size and R_{ig} is the global source term. For diffusion-limited reactions the rate coefficient k_g is proportional to the diffusion constant D. The standard form of the local rate laws is

$$\frac{\partial}{\partial t} \rho_i(\mathbf{r}, t) = D\, \nabla^2 \rho_i(\mathbf{r}, t) - k_l \rho_{\mathrm{A}}(\mathbf{r}, t)\, \rho_{\mathrm{B}}(\mathbf{r}, t) + R_{il}(\mathbf{r}, t) \tag{1.4}$$

where k_l is the time-independent local rate coefficient and the global source term $R_{ig}(t)$ is related to the local source term $R_{il}(\mathbf{r}, t)$ by a volume integral. In principle, (1.3) is the volume integral of (1.4), but in practice the nonlinear form of the reaction term makes it difficult to directly establish such a connection.(5)

2. FLUCTUATING VELOCITY FIELD

Let $n_i(\mathbf{r}, t)$ denote the local particle density of species A or B at time t. Unlike species annihilate one another upon (suitably defined) contact,

$$\mathrm{A} + \mathrm{B} \to 0 \tag{2.1}$$

We express the particle density as a sum of delta functions

$$n_i(\mathbf{r}, t) = \sum_{l=1}^{N} \delta(\mathbf{r} - \mathbf{r}_l^i(t)) \tag{2.2}$$

where $\mathbf{r}_l^i(t)$ is the location of the lth particle of type i at time t. The spatial Fourier transform

$$\hat{n}_i(\mathbf{k}, t) = \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} n_i(\mathbf{r}, t) \tag{2.3}$$

has the inverse transform (with $L^d = V =$ system volume)

$$n_i(\mathbf{r}, t) = \frac{1}{L^d} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{n}_i(\mathbf{k}, t)$$

$$\xrightarrow[L\to\infty]{} \frac{1}{(2\pi)^d} \int d\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{n}_i(\mathbf{k}, t) \tag{2.4}$$

Thus, we can write

$$n_i(\mathbf{r}, t) = \frac{1}{L^d} \sum_{\mathbf{k}} \sum_{l=1}^{N} \exp\{i\mathbf{k}\cdot[\mathbf{r} - \mathbf{r}_l^i(t)]\} \tag{2.5}$$

where the instantaneous position of the lth particle of type i is given by

$$\mathbf{r}_l^i(t) = \mathbf{r}_l^i + \int_0^t \mathbf{V}(t')\, dt' \tag{2.6}$$

Here $\mathbf{r}_l^i$ is the initial location of the lth particle and $\mathbf{V}(t)$ is the time-dependent velocity of the ambient fluid in which the chemical species i is embedded. In the absence of chemical reactions, molecular diffusion, and source terms, the time derivative of (2.5) using (2.6) yields

$$\frac{\partial}{\partial t} n_i(\mathbf{r}, t) + \mathbf{V}(t)\cdot\nabla n_i(\mathbf{r}, t) = 0 \tag{2.7}$$

The spatially-independent velocity field acts to convect the chemical species.

A microscopic description of the reaction system (2.1) would involve the description of the joint evolution of all the A and B particles present in the system (note that this number changes in time due to the reactions). This level of description is not only practically impossible, but is also unnecessarily detailed. A desirable mesoscopic level of description that yields both spatial and temporal information includes the evolution of the (suitably coarse-grained) local densities $\rho_A(\mathbf{r}, t)$ and $\rho_B(\mathbf{r}, t)$. Such local densities are first moments of the joint distribution function of all the particles, and it is unlikely that their evolution is expressible in terms of functionals of only these densities. In the present situation this includes an average over the velocity fluctuations. The evolution of the particle density including molecular diffusion and the velocity field above is

$$\frac{\partial}{\partial t} n_i(\mathbf{r}, t) + \mathbf{V}(t)\cdot\nabla n_i(\mathbf{r}, t) = D\,\nabla^2 n_i(\mathbf{r}, t) \tag{2.8}$$

Indicating the average over the velocity distribution by an overbar, we define

$$\rho_i(\mathbf{r}, t) = \frac{\overline{n_i(\mathbf{r}, t)}}{N} \tag{2.9}$$

so that (2.8) yields

$$\frac{\partial}{\partial t}\rho_i(\mathbf{r}, t) + \frac{1}{N}\overline{\mathbf{V}(t)\cdot\nabla n_i(\mathbf{r}, t)} = D\,\nabla^2\rho_i(\mathbf{r}, t) \tag{2.10}$$

To evaluate the correlation function in (2.10), we must specify the statistics of the velocity field.

Herein we concentrate on a statistical flow field because traditionally the models for turbulent fluid flow have emphasized the statistical character of the velocity field.(6) Even though the velocity field depicted in (2.8) does not have a spatial component, and therefore does not satisfy the Navier–Stokes equation, we wish to endow it with the statistical properties necessary to capture the essential features of "turbulent diffusion." Fully developed "homogeneous" turbulence involves spatial and temporal features covering many scales and no satisfactory description of its dynamic exists. However, it is well known that the diffusion of a passive scalar, such as smoke, dye, or a chemical, in a turbulent flow field leads to a mean square separation of two passive scalar particles initially close together that increase as the cube of time, i.e., $\langle R^2; t\rangle \sim t^3$.(7) This rate of separation is vastly greater than molecular diffusion, which only increases linearly with time.

We choose a model velocity field that mimics the effect of turbulent diffusion on the single-particle density function. Note that if we choose zero-centered Gaussian statistics for the model velocity field with the correlation function for the components of the velocity field(8)

$$\overline{V_m(t)\,V_n(t')} = 2\sigma_m^2\,|t-t'|\,\delta_{m,n}; \qquad m, n = x, y, z \tag{2.11}$$

then, using (2.5), we obtain

$$\overline{\mathbf{V}(t)\cdot\nabla n_i(\mathbf{r}, t)} = -3\sigma^2 t^2\,\nabla^2\overline{n_i(\mathbf{r}, t)} \tag{2.12}$$

if $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \sigma^2$. Thus we can write (2.10) as

$$\frac{\partial}{\partial t}\rho_i(\mathbf{r}, t) = K(t)\,\nabla^2\rho_i(\mathbf{r}, t) \tag{2.13}$$

where the time-dependent diffusion coefficient is

$$K(t) = D + 3\sigma^2 t^2 \tag{2.14}$$

We see from (2.14) that the "turbulent" part of the diffusion coefficient quickly dominates molecular diffusion due to its time dependence.

Note that (2.13) has the form proposed by Batchelor(9) for the relative diffusion between two particles, even though (2.13) is the evolution equation for the single-particle density.

3. REACTION-DIFFUSION EQUATION

We now write the reaction-diffusion equations incorporating the model velocity field discussed in the preceding section:

$$\frac{\partial \rho_A}{\partial t}(\mathbf{r}, t) = K_A(t)\,\nabla^2 \rho_A(\mathbf{r}, t) - F(\rho_A, \rho_B) \tag{3.1a}$$

$$\frac{\partial \rho_B}{\partial t}(\mathbf{r}, t) = K_B(t)\,\nabla^2 \rho_B(\mathbf{r}, t) - F(\rho_A, \rho_B) \tag{3.1b}$$

where the local reaction is described by the symmetric function $\mathbf{F}(\rho_A, \rho_B) = F(\rho_B, \rho_A)$. The form often taken for the reaction term is the product(4)

$$F(\rho_A, \rho_B) = k_l \rho_A(\mathbf{r}, t)\, \rho_B(\mathbf{r}, t) \tag{3.2}$$

Herein we simply accept (3.1) and (3.2) as a phenomenological starting point of the analysis, leaving the remaining question about the validity of the model on microscopic and hydrodynamic grounds for the future. We need not specify the diffusion coefficients for the A and B particles, since they are both dominated by turbulent diffusion and $K_i(t)$ is essentially given by $3\sigma^2 t^2$.

Further analysis is facilitated if instead of (3.1) we work with the sum and difference variables(10–14)

$$\gamma(\mathbf{r}, t) \equiv \tfrac{1}{2}[\rho_A(\mathbf{r}, t) - \rho_B(\mathbf{r}, t)] \tag{3.3a}$$

$$\rho(\mathbf{r}, t) \equiv \tfrac{1}{2}[\rho_A(\mathbf{r}, t) + \rho_B(\mathbf{r}, t)] \tag{3.3b}$$

The advantage of these new variables is that the equation satisfied by the difference variable is linear and independent of the chemical reaction:

$$\frac{\partial \gamma}{\partial t}(\mathbf{r}, t) = K(t)\,\nabla^2 \gamma(\mathbf{r}, t) \tag{3.4}$$

$$\frac{\partial \rho}{\partial t}(\mathbf{r}, t) = K(t)\,\nabla^2 \rho(\mathbf{r}, t) - k_l[\rho^2(\mathbf{r}, t) - \gamma^2(\mathbf{r}, t)] \tag{3.5}$$

The linear diffusion equation (3.4) is easily solved exactly. In particular, our analysis requires knowledge of the quantities $\langle\gamma(\mathbf{r}, t)\rangle$ and $\langle\gamma(\mathbf{r}, t)\,\gamma(\mathbf{r}', t')\rangle$, where the brackets denote an ensemble average either over the initial spatial distribution of the particles or on the statistics of the particle source terms when they are present.

The nonlinear equations (3.5) cannot be solved explicitly, but we are able to extract information about the long-time behavior of the averages $\langle\rho(\mathbf{r}, t)\rangle$ and $\langle\rho^2(\mathbf{r}, t)\rangle$. Since the initial conditions that we consider are spatially invariant on the average, i.e., $\langle\rho_A(\mathbf{r}, 0)\rangle$ are independent of $\mathbf{r}$, the averages $\langle\rho(\mathbf{r}, t)\rangle$ and $\langle\rho^2(\mathbf{r}, t)\rangle$ are also independent of $\mathbf{r}$. This means that $\langle\rho(\mathbf{r}, t)\rangle$ is the global density $\rho(t)$ and we can thus determine its asymptotic time evolution and the global rate law it implies.

3.1. SOLUTION IN *d* DIMENSIONS WITH NO SOURCES

The solution to the linear diffusion equation for the difference variable is given by

$$\gamma(\mathbf{r}, t) = \frac{1}{L^d} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}\,\hat{\gamma}(\mathbf{k}, t) \tag{3.6}$$

where, neglecting molecular diffusion,

$$\hat{\gamma}(\mathbf{k}, t) = \hat{\gamma}(\mathbf{k}, 0)\,e^{-\sigma^2 k^2 t^3} \tag{3.7}$$

The initial condition for the difference variable is

$$\gamma(\mathbf{r}, t=0) = \frac{1}{2} \sum_{l=1}^{N} \left[\delta(\mathbf{r} - \mathbf{r}_l^{A}) - \delta(\mathbf{r} - \mathbf{r}_l^{B})\right] \tag{3.8}$$

with the Fourier transform

$$\hat{\gamma}(\mathbf{k}, t=0) = \frac{1}{2} \sum_{l=1}^{N} \left[\exp(i\mathbf{k}\cdot\mathbf{r}_l^{A}) - \exp(i\mathbf{k}\cdot\mathbf{r}_l^{B})\right] \tag{3.9}$$

Since we only require the first two moments of the difference variable, we need not determine the entire distribution for the initial state.

To calculate the average $\langle\gamma(\mathbf{r}, t)\rangle$ over the initial distribution of particles, we note that their random placement implies that

$$\langle\exp(i\mathbf{k}\cdot\mathbf{r}_l^{A})\rangle = \langle\exp(i\mathbf{k}\cdot\mathbf{r}_l^{B})\rangle = \delta_{\mathbf{k},0} \tag{3.10}$$

so that $\langle\hat{\gamma}(\mathbf{k}, 0)\rangle = 0$ and consequently $\langle\hat{\gamma}(\mathbf{k}, t)\rangle$ *and* $\langle\gamma(\mathbf{r}, t)\rangle$ also vanish for all time, reflecting the fact that if the number of A's and B's are equal initially, they remain so for all time.

To calculate the d-dimension γ-correlation function

$$C_\gamma^{(d)}(\mathbf{r}-\mathbf{r}', t) = \langle \gamma(\mathbf{r}, t)\, \gamma(\mathbf{r}', t) \rangle \tag{3.11}$$

we use (3.6) and (3.7) to write

$$C_\gamma^{(d)}(\mathbf{r}-\mathbf{r}', t) = \frac{1}{L^{2d}} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \langle \hat{\gamma}(\mathbf{k}, 0)\, \hat{\gamma}(\mathbf{k}', 0) \rangle e^{-(k^2+k'^2)\sigma^2 t^3} \times e^{-i(\mathbf{k}\cdot\mathbf{r}+\mathbf{k}'\cdot\mathbf{r}')} \tag{3.12}$$

The second moment in (3.12) is

$$\langle \hat{\gamma}(\mathbf{k}, 0)\, \hat{\gamma}(\mathbf{k}', 0) \rangle = \frac{N}{2} \delta_{\mathbf{k}+\mathbf{k}',0} \tag{3.13}$$

when the two species are mutually uncorrelated in the initial state. Substituting (3.13) into (3.12) and using $\rho_0 \equiv N/V$ yields in d dimensions

$$C_\gamma^{(d)}(\mathbf{r}-\mathbf{r}', t) = \frac{\rho_0}{2(8\pi\sigma^2 t^3)^{d/2}} e^{-(\mathbf{r}-\mathbf{r}')^2/8\sigma^2 t^3} \tag{3.14}$$

Thus the mean square value of the difference variable decays in time as $t^{-3d/2}$:

$$\langle \gamma^2(\mathbf{r}, t) \rangle = \frac{\rho_0}{2(8\pi\sigma^2 t^3)^{d/2}} \tag{3.15}$$

This time dependence is quite different than the $t^{-d/2}$ obtained by a number of other authors(14, 15) for diffusion-dominated systems in the absence of the velocity field.

Let us now examine the behavior of the sum variable in (3.5). Consider the average of (3.5) over the initial distribution of A's and B's:

$$\frac{\partial}{\partial t} \langle \rho(\mathbf{r}, t) \rangle = K(t) \nabla^2 \langle \rho(\mathbf{r}, t) \rangle - k_l [\langle \rho^2(\mathbf{r}, t) \rangle - \langle \gamma^2(\mathbf{r}, t) \rangle] \tag{3.16}$$

Although we cannot solve (3.16) exactly, we can infer the leading time dependence of the averages.(4, 11, 14) To do so, we assume that the leading time contribution to $\langle \rho^2 \rangle$ is the square of the leading contribution to $\langle \rho \rangle$. The diffusion term vanishes, since our initial conditions assume that $\langle \rho \rangle$ is independent of the absolute position $\mathbf{r}$. Thus,

$$\langle \rho \rangle \sim t^{-\alpha}, \qquad \langle \rho^2 \rangle \sim t^{-2\alpha}, \qquad \frac{\partial}{\partial t} \langle \rho \rangle \sim t^{-\alpha-1} \tag{3.17}$$

Schematically we can then write (3.16) as

$$t^{-\alpha-1} \sim t^{-2\alpha} - t^{-2\mu} \tag{3.18}$$

where μ is known from our earlier calculation to be $3d/4$, and the diffusion term vanishes due to the spatial independence of $\langle \rho(\mathbf{r}, t) \rangle$.

If μ is smaller than unity, then the only way to balance the leading time dependence in (3.18) is to have $\alpha = \mu$. If, on the other hand, $\mu > 1$, then a balance is achieved by choosing $\alpha + 1 = 2\alpha$, i.e., $\alpha = 1$. The former case leads to anomalous (slow) decay of the global density, while the latter is the classical textbook case.

For uncorrelated initial conditions we found in (3.15) that $\mu = 3d/4$ and hence for $d \leqslant 4/3$ we set $\alpha = 3d/4$, while for $d > 4/3$ we have $\alpha = 1$:

$$\langle \rho(\mathbf{r}, t) \rangle = \rho(t) \sim \begin{cases} t^{-3d/4}, & d \leqslant 4/3 \\ t^{-1}, & d > 4/3 \end{cases} \tag{3.19}$$

In this way we see that an anomolous reaction rate occurs in one dimension even with mixing present, but not for $d \geqslant 4/3$.

3.2. SOLUTION IN *d*-DIMENSIONAL VOLUMES WITH SOURCES

We include sources for the chemical species in our discussion by modifying (3.4) and (3.5) in the following way:

$$\frac{\partial \gamma}{\partial t}(\mathbf{r}, t) = K(t)\,\nabla^2 \gamma(\mathbf{r}, t) + \eta_\gamma(\mathbf{r}, t) \tag{3.20a}$$

$$\frac{\partial \rho}{\partial t}(\mathbf{r}, t) = K(t)\,\nabla^2 \rho(\mathbf{r}, t) - k_l[\rho^2(\mathbf{r}, t) - \gamma^2(\mathbf{r}, t)] + \eta_\rho(\mathbf{r}, t) \tag{3.20b}$$

where the random source terms η_γ and η_ρ are defined in analogy with (3.3) as sum and difference variables. The average number of A and B molecules is kept equal at all times, i.e.,

$$\int d\mathbf{r}\; \rho_A(\mathbf{r}, 0) = \int d\mathbf{r}\; \rho_B(\mathbf{r}, 0) \tag{3.21a}$$

$$\int d\mathbf{r}\; \langle \eta_A(\mathbf{r}, t) \rangle = \int d\mathbf{r}\; \langle \eta_B(\mathbf{r}, t) \rangle \tag{3.21b}$$

so that

$$\int d\mathbf{r}\; \langle \gamma(\mathbf{r}, t) \rangle = \int d\mathbf{r}\; \langle \eta_\gamma(\mathbf{r}, t) \rangle = 0 \tag{3.22}$$

at all times.

As in the preceding section, we wish to evaluate the first and second moments of $\gamma(\mathbf{r}, t)$, but in the case when there are no A and B particles present in the fluid initially and the source terms are stochastic. Therefore, to calculate these moments, we must specify the statistical properties of the sources; in particular, because of the linearity of (3.20a), we need only specify the first and second moments $\langle \eta_\gamma(\mathbf{r}, t) \rangle$ and $\langle \eta_\gamma(\mathbf{r}, t)\, \eta_\gamma(\mathbf{r}', t') \rangle$. We consider only sources that are spatially invariant on the average so that $\langle \gamma(\mathbf{r}, t) \rangle$ is independent of $\mathbf{r}$ and hence is the global difference variable $\gamma(t)$, and $\langle \gamma(\mathbf{r}, t)\, \gamma(\mathbf{r}', t') \rangle$ depends only on the differences $\mathbf{r} - \mathbf{r}'$ and $t - t'$.

We restrict our discussion here to strictly conservative sources, i.e., at all times the number of A's deposited in the fluid is exactly equal to the number of B's deposited, albeit at random locations whose distribution must still be specified. We envision the deposition process as follows: A (or B) particles are deposited from a source at a point at the rate of one particle per unit time τ, after which that particular source is turned off (or moved elsewhere). At time t, $N_\mathrm{A}(t)$ A particles per unit time are being deposited in this way in the entire system, so that the deposition rate of A's per unit volume at time t is $\eta_\mathrm{A}(t) = N_\mathrm{A}(t)/L^d$. For strictly conservative sources, $\langle \eta_\mathrm{A}(t) \rangle = \langle \eta_\mathrm{B}(t) \rangle$ at all times, so that $\langle \eta_\gamma(t) \rangle = 0$.

Let us now consider the difference variable. Fourier-transforming (3.20a) and integrating the transformed equation over time subject to the initial condition $\gamma(\mathbf{r}, t=0) = \hat{\gamma}(\mathbf{k}, t=0) = 0$ gives

$$\hat{\gamma}(\mathbf{k}, t) = \int_0^t dt'\, e^{-\sigma^2 k^2 (t^3 - t'^3)} \hat{\eta}_\gamma(\mathbf{k}, t') \tag{3.23}$$

For strictly conservative sources

$$\langle \hat{\eta}_\gamma(\mathbf{k}, t) \rangle = 0 \tag{3.24}$$

and hence

$$\langle \hat{\gamma}(\mathbf{k}, t) \rangle = 0 \tag{3.25}$$

i.e., the system contains an equal number of A and B particles at all times. To evaluate the correlation function $\langle \gamma(\mathbf{r}, t)\, \gamma(\mathbf{r}', t') \rangle$, we note from (3.23) that

$$\begin{aligned} &\langle \hat{\gamma}(\mathbf{k}, t)\, \hat{\gamma}(\mathbf{k}', t') \rangle \\ &\quad = \int_0^t dt_1 \int_0^{t'} dt_2 \exp[-\sigma^2 k^2 (t^3 - t_1^3)] \exp[-\sigma^2 k'^2 (t'^3 - t_2^3)] \\ &\qquad \times \langle \eta_\gamma(\mathbf{k}, t_1)\, \eta_\gamma(\mathbf{k}', t_2) \rangle \end{aligned} \tag{3.26}$$

where the source correlation function is yet to be specified. For uncorrelated particles in the source we obtain[4]

$$\langle \hat{\eta}_\gamma(\mathbf{k}, t_1)\, \hat{\eta}_\gamma(\mathbf{k}', t_2) \rangle = 2RL^d \delta_{\mathbf{k}+\mathbf{k}',0}\, \delta(t_1 - t_2) \tag{3.27}$$

where R is the time-independent deposition rate for both chemical species. Thus we may write

$$\langle \hat{\gamma}(\mathbf{k}, t)\, \hat{\gamma}(\mathbf{k}', t) \rangle = 2RL^d \delta_{\mathbf{k}+\mathbf{k}',0} \int_0^t dt'\, e^{-2\sigma^2 k^2 (t^3 - t'^3)} \tag{3.28}$$

and we obtain for the γ-correlation function in d dimensions [cf. (3.11)]

$$C_\gamma^{(d)}(\mathbf{r} - \mathbf{r}', t) = \frac{R}{L^d} \sum_{\mathbf{k} \neq 0} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} \int_0^t dt'\, e^{-2\sigma^2 k^2 (t^3 - t'^3)} \tag{3.29}$$

We replace the $\mathbf{k}$ sum in (3.29) with an integral over wave vectors

$$\frac{1}{L^d} \sum_{\mathbf{k} \neq 0} \rightarrow \frac{1}{(2\pi)^d} \int d\mathbf{k} \tag{3.30}$$

so that

$$C_\gamma^{(d)}(\mathbf{X}, t) = \frac{R}{(2\pi)^d} \int_0^t dt' \int d\mathbf{k}\, e^{i\mathbf{k} \cdot \mathbf{X}} e^{-2\sigma^2 k^2 (t^3 - t'^3)} \tag{3.31}$$

where $\mathbf{X} = \mathbf{r} - \mathbf{r}'$.

The γ-correlation function is evaluated by first doing the $\mathbf{k}$ integration in each dimension and then explicitly carrying out the time integration. This is done explicitly in the Appendix, where $C_\gamma^{(d)}$ is expressed in terms of Kummer functions. In Fig. 1 we depict scaled forms of the correlation

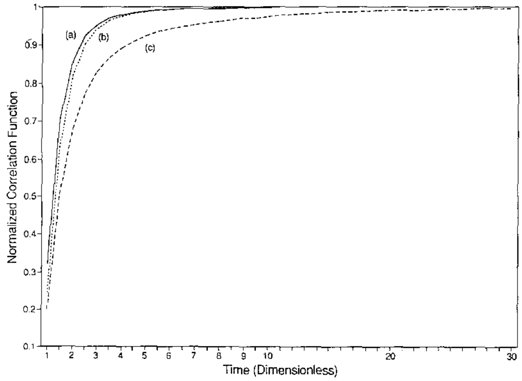

Fig. 1. The scaled γ-correlation functions $C_\gamma^{(d)}$ as a function of the dimensionless time τ: (a) $\tau C_\gamma^{(1)}$ (---), (b) $\tau^2 C_\gamma^{(2)}/\ln \tau$ (···), and (c) $\tau^2 C_\gamma^{(3)}$ (——).

functions as a function of the dimensionless "time" variable $\tau = (8\sigma^2/r^2)^{1/3}t$ and r is the appropriate distance variable in one, two, and three dimensions. From the figure we see that $\sqrt{\tau}\, C_\gamma^{(1)} \to \text{const}$ as τ becomes large, indicating an asymptotic time dependence of $C_\gamma^{(1)} \sim t^{-1/2}$. This decay is in marked distinction to the situation when mixing is not present, in which case $\langle \gamma^2 \rangle \sim t^{1/2}$.

Again balancing the terms in the reaction-diffusion equation to estimate the time dependence of the sum variable, we have with the additional effect of the source term

$$t^{-\alpha-1} \sim t^{-2\alpha} - t^{-2\mu} + t^0 \tag{3.32}$$

where -2μ is the exponent of the time in $\langle \gamma^2 \rangle$ and is in this case equal to $-1/2$. It is clear that we must then have $\alpha = 1/4$:

$$\langle \rho(\mathbf{r}, t) \rangle = \rho(t) \sim t^{-1/4}, \qquad d = 1 \tag{3.33}$$

We can also see from Fig. 1 that $\tau^2 C_\gamma^{(2)}/\ln \tau \to \text{const}$ with increasing τ. The asymptotic time dependence of $C_\gamma^{(2)}$ is therefore $\ln t/t^2$ and the average concentration has

$$\rho(t) \sim (\ln t)^{1/2}/t, \qquad d = 2 \tag{3.34}$$

as its time dependence. Again the average concentration decays, unlike the case without the random mixing, where $\rho(t) \sim (\ln t)^{1/2}$.

Finally we see from Fig. 1 that in three dimensions the scaled correlation function $\tau^2 C_\gamma^{(3)} \to \text{const}$ as $\tau \to \infty$. Therefore $C_\gamma^{(3)}$ has the asymptotic time dependence t^{-2} and the sum concentration has the classical time dependence

$$\rho(t) \sim t^{-1}, \qquad d \geqslant 3 \tag{3.35}$$

Note that the unmixed case had a constant for the average concentration in three dimensions.

4. SUMMARY

Herein we have studied a model in which a spatially independent stochastic model of a velocity field was introduced as a mixing mechanism for the A + B → 0 chemical reaction. The statistics of the velocity field was chosen to mimic turbulent diffusion and resulted in an enhanced rate of chemical reaction. In the case of no sources and a random distribution of an equal number of A's and B's in the initial state the global reaction rate was found to be [cf. (3.19)]

$$\frac{d\rho}{dt}(t) \sim -\rho^{(3d+4)/3d}, \qquad d \leqslant 4/3$$
$$\sim -\rho^2, \qquad d \geqslant 4/3 \tag{4.1}$$

Unlike results obtained earlier, we see that the effect of "turbulent mixing" is to suppress chemical segregation for $d \geqslant 4/3$, in which case the global rate law is the classical one.

The situation is again different when the chemical species are continuously fed into the system at random locations. The global rate laws are

$$\frac{d\rho(t)}{dt} \sim \begin{cases} -\rho^{4/5}, & d=1 \\ F(\rho, t), & d=2 \\ -\rho^2, & d \geqslant 3 \end{cases} \tag{4.2}$$

where the form of $F(\rho, t)$ obtained from (3.34) is not particularly informative except insofar as it is not of the classical form. Of most interest is the result for $d \geqslant 3$, which states that the classical global reaction rate is the appropriate description of the $A + B \rightarrow 0$ reaction in the presence of turbulent mixing.

Thus, the model for turbulent mixing used here washes out the effects of spatial inhomogeneities in the reaction-diffusion equations and gives rise to the classical global reaction rate laws in three dimensions.

APPENDIX. EVALUATION OF CORRELATION FUNCTION

The correlation function can also be written as

$$C_\gamma^{(d)}(\mathbf{X}, t) = \frac{R}{(2\pi)^d} \int_0^t A_d(\mathbf{X}; t; t')\, dt' \tag{A1}$$

where

$$A_d(\mathbf{X}; t, t') \equiv \int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{X} - k^2 a^2} \tag{A2}$$

and we have found it convenient top introduce the distance parameter

$$a^2 \equiv 2\sigma^2(t^3 - t'^3) \tag{A3}$$

The properties of the correlation function in one, two, and three dimensions can be determined from those of A_1:

$$A_1(X; t, t') = \int_{-\infty}^{\infty} e^{ikX} e^{-a^2k^2}\, dk \tag{A4}$$

which integrates to

$$A_1(x; t, t') = \left[\frac{\pi}{2\sigma^2(t^3 - t'^3)}\right]^{1/2} \exp\left\{-\frac{X^2}{8\sigma^2(t^3 - t'^3)}\right\} \tag{A5}$$

Thus in one dimension the correlation function (A1) is

$$C_\gamma^{(1)}(X, t) = \frac{R}{2(2\pi\sigma^2)^{1/2}} \int_0^t \frac{dt'}{(t^3 - t'^3)^{1/2}} \exp\left\{-\frac{X^2}{8\sigma^2(t^3 - t'^3)}\right\} \tag{A6}$$

which in terms of the scaled variable ($t \geqslant 0$)

$$\eta = \frac{t^3}{t^3 - t'^3} \tag{A7}$$

can be written

$$C_\gamma^{(1)}(x, t) = \frac{R}{6(2\pi\sigma^2 t)^{1/2}} \int_1^\infty \frac{e^{-\alpha\eta}\, d\eta}{\eta^{5/6}(\eta - 1)^{2/3}} \tag{A8}$$

where in terms of the Kummer function U

$$C_\gamma^{(1)}(X, t) = \frac{R}{6(2\pi\sigma^2 t)^{1/2}} \Gamma\left(\frac{1}{3}\right) e^{-\alpha} U\left(\frac{1}{3}, \frac{1}{2}, \alpha\right) \tag{A9}$$

with $\alpha = X^2/8\sigma^2 t^3$.

In a similar way we may evaluate the appropriate integrals for the two-dimensional case:

$$\begin{aligned} A_2(X, Y; t, t') &= \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y \exp(ik_x X - a^2k_x^2) \exp(ik_y Y - a^2k_y^2) \\ &= A_1(X; t, t')\, A_1(Y; t, t') \end{aligned} \tag{A10}$$

where $X = x - x'$ and $Y = y - y'$; so that A_2 is the direct two-dimensional Gaussian with a dispersion growing cubically in time. The two-dimensional correlation function is

$$C_\gamma^{(2)}(X, Y, t) = \frac{R}{2\pi\sigma^2 t^2} \int_1^\infty \frac{e^{-\beta\eta}\, d\eta}{\eta^{1/3}(\eta - 1)^{2/3}} \tag{A11}$$

where $\beta = (X^2 + Y^2)/8\sigma^2 t^3$, so that

$$C_\gamma^{(2)}(X, Y, t) = \frac{R}{24\pi\sigma^2 t^2}\,\Gamma\left(\frac{1}{3}\right) e^{-\beta} U\left(\frac{1}{3}, 1, \beta\right) \tag{A12}$$

Finally, we can write

$$C_\gamma^{(3)}(X, Y, Z, t) = \frac{R\Gamma(1/3)}{3\sigma^2(8\pi)^{3/2}}\,\frac{e^{-\gamma}}{t^{7/2}}\, U\left(\frac{1}{3}, \frac{3}{2}, \gamma\right) \tag{A13}$$

where $\gamma = (X^2 + Y^2 + Z^2)/8\sigma^2 t^3$.

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