EFFECTIVE RATES IN DILUTE REACTION-ADVECTION SYSTEMS

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Abstract A dilute system of reacting particles transported by fluid flows is considered. The particles react as $A+A \to \varnothing$ with a given rate when they are within a finite radius of interaction. The system is described in terms of the joint n-point number spatial density that obeys a hierarchy of transport equations. An analytic solution is obtained in either the dilute or the long-time limit by using a Lagrangian approach where statistical averages are performed along non-reacting trajectories. In this limit, it is shown that the moments of the number of particles have an exponential decay rather than the algebraic prediction of standard mean-field approaches. The effective reaction rate is then related to Lagrangian pair statistics by a large-deviation principle. Numerical simulations in a smooth, compressible, random delta-correlated-in-time Gaussian velocity field support the theoretical results.

Many natural and industrial processes involve the reaction or collision of diffusing species transported by an outer turbulent flow. Such systems are typically modeled in terms of the *reaction-diffusion-advection* equation for the density field ρ. In the simple case of the pair-annihilation reaction $A+A \to \varnothing$, where two molecules react together to become inert, this kinetic equation takes the form

$$\partial_t \rho + \nabla \cdot (\rho \vec{v}) = -\Gamma \rho^2 + \kappa \nabla^2 \rho, \tag{1}$$

where κ is the diffusion constant, $\vec{v}$ the velocity of the outer flow, and Γ the reaction rate. An important aspect withheld in such an approach is the assumed relation between the microscopic stochastic rate, that is the probability that two given individual molecules react, and the mesoscopic reaction propensity, that is the number of reactions per unit time and volume written here as $\Gamma\rho^2$. To derive (1) one must assume two properties to be satisfied at the coarse-graining scale from which the hydrodynamic limit is taken. First, volumes at the coarse-graining scale have to contain sufficiently many particles, in order to safely disregard finite-number fluctuations. Second, each particle within this volume must have an equal probability to react with all the others — *well-mixing* hypothesis. It is clear that in situations where the reactants are very dilute, the two conditions underlying (1) might not be simultaneously satisfied. In particular, fluctuations due to a finite number of reactants might be so important to invalidate the mean-field assumptions leading to (1). Much work has been devoted to model and study such fluctuations in situations where transport is negligible and diffusion dominates. It was shown that finite-number effects can be taken into account by adding an imaginary noise in the reaction-diffusion equation [6]. Such approaches, which were developed for diffusion-limited reactions, cannot be straightforwardly extended to cases where transport cannot be neglected. This is the case for instance of water droplets in clouds growing by coalescense [5] or of phytoplankton confined in a two-dimensional ocean layers [4]. Because of the large sizes of the transported species, molecular diffusion is negligible in all aforementioned examples. The aim of this work is to develop a general framework which can be used to address such issues. Particular interest is devoted to determine an effective reaction rate taking into account diluteness and fluctuations of the carrier flows.

We consider a set of reacting particles $\{A_i\}_{1\le i\le N(t)}$ located at $\vec{X}_i$ obeying the following dynamics and binary reaction

$$\frac{\mathrm{d}\vec{X}_i}{\mathrm{d}t} = \vec{v}(\vec{X}_i,t), \text{ reacting as } A+A \xrightarrow{\mu} \varnothing \text{ when } |\vec{X}_i - \vec{X}_j| < a, \tag{2}$$

with a the interaction radius and μ the microscopic rate. The d-dimensional velocity field $\vec{v}$ is assumed to be differentiable with given isotropic, stationary, and homogeneous statistics. Also, we assume that $\vec{v}$ is compressible and has a finite correlation time. In addition, the dynamics is assumed ergodic, chaotic and defined in a bounded domain. The trajectories generated by (2) will then concentrate on a dynamically evolving strange attractor (see, e.g., [2]). We suppose that the radius of interaction a is smaller than the scale at which $\vec{v}$ varies (e.g smaller than the Kolmogorov length scale for a turbulent flow).

The starting point to describe such system is to introduce the joint n-point number density,

$$\mathscr{F}_n(\vec{x}_1,\dots,\vec{x}_n,t) = \left\langle \sum_{i_1\neq\dots\neq i_n}^{N(t)} \delta\left(\vec{X}_{i_1}(t)-\vec{x}_1\right)\cdots\delta\left(\vec{X}_{i_n}(t)-\vec{x}_n\right)\right\rangle_\mu, \tag{3}$$

where the brackets $\langle\cdot\rangle_\mu$ stands for the ensemble average with respect to reactions only and, by convention, the sum in (3) is zero when $N(t)<n$. When $\mathscr{F}_n(\vec{x}_1,\dots,\vec{x}_n,t)$ is integrated over all spatial variables it gives the mean value of the factorial moments of the number of particles $N(t)$ present at time t. In [3], it was shown that (3) satisfies a hierarchy of transport equations that can be formally solved by using Lagrangian trajectories. In particular it is possible to show that

all moments of the number of particles decrease exponentially with the same rate as $\langle N^p \rangle_\mu \sim \mathrm{e}^{-\gamma t}$. This was corroborated by Monte-Carlo simulations. Note that this behavior strongly differs from the $\propto t^{-p}$ mean-field prediction. The long-time dynamics is thus dominated by the temporal evolution of the number of pair $n_2(t)$. It can be expressed in terms of the relative distance $R(t)$ of two (non reacting) Lagrangian trajectories (see [3] for details) as

$$n_2(t) \propto \overline{\mathrm{e}^{-\mu \int_0^t \theta(a-R(s))\,\mathrm{d}s}}, \tag{4}$$

where the over-bar denotes the average over all realizations of the carrier velocity field $\vec{v}$. The long-time asymptotics of n_2 requires to understand the behavior of the fraction of time $\Theta = (1/t)\int_0^t \theta(a-R(s))\,\mathrm{d}s$ that two particles spend at a distance smaller than a. Under ergodicity hypotheses on the two-point dynamics, this self-averaging quantity converges at long times to $P_2^<(a)$, the probability of finding two particles at distance less than a. When the dynamics is sufficiently mixing, the deviations of Θ from its average are described by a large-deviation principle [1]. The probability density function $p(\Theta)$ thus has the asymptotic behavior $p(\Theta) \sim \exp[-t\mathscr{H}(\Theta)]$, where $\mathscr{H}$ is a convex positive rate function, which attains its minimum, equal to zero, at $\Theta = P_2^<(a)$. Using $p(\Theta)$ in (4) and a saddle-point approximation leads to the following expression for the effective rate γ

$$\gamma = -\lim_{t\to\infty} \frac{1}{t} \ln n_2(t) = \inf_{\Theta \geq 0} [\mu\,\Theta + \mathscr{H}(\Theta)]. \tag{5}$$

The convexity of $\mathscr{H}$ implies that γ is a non-decreasing function of μ. Furthermore, the asymptotic behaviors of γ can be inferred from general properties of $\mathscr{H}$. Indeed, for small μ the effective rate is given by the values of $\mathscr{H}(\Theta)$ near its minimum, so that $\gamma \simeq \mu\, P_2^<(a) - \mu^2\,\sigma^2/2$, with σ^2/t the variance of Θ. This results is a direct consequence of the central-limit theorem. On the other hand, for $\mu \to \infty$, γ saturates to the value $\gamma_\infty = \mathscr{H}(0) = 1/\overline{T_{\mathrm{hit}}}$, where $\overline{T_{\mathrm{hit}}}$ is the mean time taken by two trajectories initially far away to be at a distance a for the first time. Numerical simulations using a $2-$dimensional smooth and compressible Kraichan flow confirm these predictions. Figure 1 shows the full dependence of the rate γ (and γ/μ) on the microscopic rate μ in perfect agreement with the asymptotic results. In reference [3],

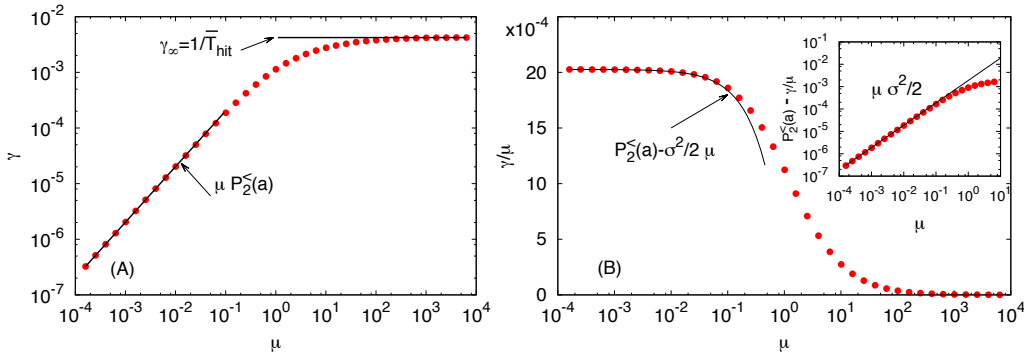

Figure 1. Effective reaction rate γ for the Kraichnan flow. Compressibility $\wp = 0.1$ and interaction radius $a/L = 5\cdot 10^{-3}$ (L is the size of the domain). (A) γ vs μ, the solid lines shows the small and large μ asymptotics. (B) γ/μ vs μ, the solid line displays the central-limit theorem prediction, which is made more clear in the inset by eliminating the constant term.

a phenomenological model was introduced allowing to compute the rate function $\mathscr{H}$ and to express γ in terms of the correlation dimension and the largest Lyapunov exponent of the Lagrangian flow. Furthermore, for the Kraichan flow, assuming a log-normal distribution for $R(t)$ and using some properties of the Brownian motion with drift an explicit expression for γ was found to be in good quantitative agreement with numerical simulations.

The formalism developed in this work allows one to describe the dynamics of a dilute system of reacting particles transported by a compressible flow. It can be straightforwardly extended to a more general particle dynamics, as inertial or charged particles, and to more general kind of reactions.

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