# Micromixing Effects on Autocatalytic Reactions in a Stirred Tank: The Random Replacement IEM Model

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The random replacement interaction-by-exchange-with-the-mean (IEM) model, which was proposed previously as a numerically more preferable IEM scheme, had been employed for investigating the micromixing effects on the steady-state multiplicity and the relative stability of the oscillatory and stationary state of the Gray−Scott model (Gray, P.; Scott, S. K. *Chem. Eng. Sci.* **1983**, *38*, 29). In the bistable region, incomplete micromixing tends to largely reduce the attraction basin for the thermodynamic branch, while in the region where the stable limit cycle exists, it tends to weaken the relative stability of the oscillatory states. Owing to the random replacement nature of the present micromixing model, a stochastic response behavior is observed for the resulting limit cycle attractor and the attraction basin boundary on the parameter space.

## Introduction

Incomplete mixing can quantitatively or even qualitatively alter the complex system dynamics when the mixing time is comparable to the reaction characteristic time.[1,2] The importance of mixing is usually discussed in terms of macromixing and micromixing. Macromixing involves the hydrodynamic aspect in the reactor, while various geometrical factors such as reactor shape, stirrer type, or the presence of baffles all markedly affect the macromixing. On the other hand, micromixing involves the related processes with scales below the turbulence characteristic length. The effects of incomplete macromixing on complex chemical dynamic systems have been investigated by some works.[3−11] Zonal models are widely employed in these studies. The micromixing effects had attracted certain research interests as well.[12−26] The most widely employed micromixing models include the coalescence-dispersion (CD) model and the interaction-by-exchange-with-the-mean (IEM) model. The IEM model had attracted a great research interest owing to its simplicity and containing only one adjustable parameter.[1,24]

The basic idea underlying the IEM model is to assume the existence of many small fluid particles in the tank and a mean concentration field to exchange mass with. The mean concentration is defined as a weighted average of particle concentration based on the lifetime distribution of the particles (an exponential-type distribution for a well-macromixed tank), while the mass exchange rate is assumed inversely proportional to a characteristic mixing time $t_m$. By discussing the time evolution of reactants in all particles and the mean field concentration at fixed time interval, and further considering the particle inflow/outflow terms, the completeness of micromixing can be studied by varying $t_m$. A smaller $t_m$ indicates a more complete micromixing.

A modified, unsteady-state version of the IEM model has later been developed to incorporate the dynamic behaviors of chemical systems and had been successfully employed in various chemical systems, including the classical chlorite−iodide bistable/oscillatory systems.[19,24] However, the conventional numerical scheme is not suitable for the systems with a stiff time evolution, such as the Oregonator.

To overcome this difficulty, a so-called random replacement IEM model (abbreviated as the R$_2$IEM model hereinafter) had been proposed recently.[27] The major difference between the R$_2$IEM model and the original IEM model is the adoption of a scheme similar to the molecular dynamics (MD) simulation, with which we can work directly on the absolute time scale. By repeatedly random replacement of a fluid particle from the stirred tank with a fresh fluid particle, a stationary residence time distribution of exponential-type can be achieved no matter what the initial lifetime distribution is (as shown in later sections). The mean concentration can thereby be taken as an average over all the existing particles in the tank regardless of their age. This scheme has been shown equivalent to the conventional IEM model when the fluid particle number is large, however, and has avoided the necessity for numerical evaluation of the integrand involved. This makes the R$_2$IEM model a numerically more preferable scheme, especially for systems with a stiff time evolution.

The Gray−Scott (G−S) model is one of the simplest nonlinear kinetic models exhibiting both the bistable and oscillatory dynamic behavior.[28−30] The G−S model corresponds to the chemical reactions as follows:

$$U + 2V \rightarrow 3V \tag{1}$$

$$V \rightarrow \text{product} \tag{2}$$

The corresponding dynamical dimensionless equations with feed concentrations (1.0, 0.0) are given by Pearson:[31]

$$\mathrm{d}U/\mathrm{d}t = -UV^2 + F(1 - U) \tag{3}$$

$$\mathrm{d}V/\mathrm{d}t = UV^2 - (F + k)V \tag{4}$$

It is an abstract scheme but reveals key aspects of many real systems.[32] The effects of macromixing on the relative stability of the bistable and the oscillatory attractors for the G−S model had been investigated recently.[11] The so-called "well-macromixing limit" was addressed. The major role of incomplete macromixing is found to alter the relative stability between the stationary and the oscillatory states. The focus of this report is to employ the newly proposed R$_2$IEM model for investigating the bistability and oscillatory states for the Gray−Scott model and the possibility in inducing chaotic behavior. A brief description of the R$_2$IEM model is given first in the next section.

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## The Models

**Random Replacement IEM Model.** The basic difference between the $R_2$IEM model and the conventional IEM models is that the former works on the absolute time scale with the average concentration over the whole tank taken as

$$\langle \mathbf{C} \rangle = (1/N)\sum_{i=1}^{N}\mathbf{C}_i \tag{5}$$

where $\mathbf{C}_i = [U_i,V_i]^{\mathrm{T}}$ is the concentration vector for the $i$th fluid particle and $N$ is the total particle number. The validity for adopting eq 5 is underlying the assurance of a prescribed lifetime distribution of fluid particles in the tank. For a well-macromixed tank, the lifetime distribution of the fluid particles in the tank with a mean residence time $\tau$ ($=1/F$, $F$ is the reduced flow rate) is

$$E(\alpha) = \exp(-\alpha/\tau)/\tau \tag{6}$$

where $\alpha$ is the particle lifetime.[33] That is, there is less chance of finding an elder particle in a well-macromixed tank.

An equivalent statement for a well-macromixed tank is that an equal probability exists for all particles to leave the tank at any time.[34] This statement forms the mass inflow/outflow mechanism of the $R_2$IEM model. That is, the steady-state mass inflow/outflow of the tank is achieved by randomly selecting and replacing an existing fluid particle by a fresh particle, with an equal probability, at a time interval of $\Delta\tau$ ($=\tau/N$) regardless of its age. The age of the remaining particles of age $j\Delta\tau$ will then be increased by $\Delta\tau$, and the whole process repeated itself. If the particle lifetime distribution thus constructed is eq 6, the validity of adopting eq 5 as the mean concentration, or the $R_2$IEM model, is confirmed.

Such a process can be approximated by a continuous stochastic process, if the time interval $\Delta\tau$ is small enough. The number of particles of age $j\Delta\tau$, $n_j$, is the random variable under investigation. Since the probability for any particle to leave the tank is equal, the probability for a particle during time interval $\mathrm{d}t$ to be selected and replaced from the state $j$ is $n_j\,\mathrm{d}t/N\Delta\tau$. At the end of each time interval of $\Delta\tau$, the remaining particles in state $j$ will be moved into state $j+1$, while the fresh particles are fed into state 0 with a rate of $Q$. Take the probability of exactly $n_j$ particles existing at state $j$ as $P_j(t) = n_j/N$, where $n_j = 0, 1, ..., N$. The following probabilities hold for $j$ larger than zero

$$\frac{\mathrm{d}P_j(t)}{\mathrm{d}t} = -\frac{1}{\Delta\tau}P_j(t) + \frac{1}{\Delta\tau}\left(1 - \frac{1}{N}\right)P_{j-1}(t) \tag{7}$$

or equal to zero.

$$\frac{\mathrm{d}P_0(t)}{\mathrm{d}t} = -\frac{1}{\Delta\tau}\left(1 - \frac{1}{N}\right)P_0(t) + \frac{Q}{\tau} \tag{8}$$

From eqs 7 and 8, since $\Delta\tau$ and $N$ are both independent of time and the sum of all $P_j$'s is unity, if $N$ is large, a stationary distribution of exponential-type ($\exp(-j/N)/\tau$) of particles of age $j\Delta\tau$ will be asymptotically approached no matter what the initial lifetime distribution is, which confirms the employment of the scheme.

The above results demonstrate that, by randomly selecting and replacing particles with a fresh particle at a time interval of $\Delta\tau$ for many times, a well-macromixed condition can be guaranteed. In the present work, it is noted that a stationary, exponential-type distribution can be established for a system with 500 fluid particles by less than 2000 times of random selection and replacement. Such a pretreatment can be referred to as the "annealing" process usually adopted in molecular dynamics simulations[35] and is employed throughout the present work.

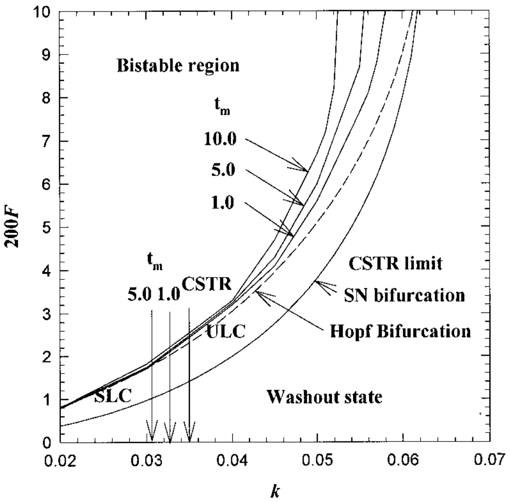

**Figure 1.** Bifurcation diagram for the Gray–Scott model under complete and incomplete micromixing: SLC, stable limit cycle; ULC, unstable limit cycle.

**Gray–Scott Model.** In each fluid particle, the evolution path for the two reactants U and V in G–S model owing to the $R_2$-IEM scheme can be evaluated as follows:

$$\frac{\mathrm{d}U_i}{\mathrm{d}t} = -U_iV_i^2 + \frac{1}{t_m}(\langle U \rangle - U_i) \tag{9}$$

$$\frac{\mathrm{d}V_i}{\mathrm{d}t} = U_iV_i^2 - kV_i + \frac{1}{t_{\mathrm{m}}}(\langle V \rangle - V_i), \quad i = 1, ..., N \tag{10}$$

with the inflow/outflow selection mechanism as described above. The calculation procedures can be summarized as follows. First, $N$ particles with prescribed initial concentrations are placed in the tank. To construct the required exponential-type particle age distribution, as discussed above, for the first 2000 $\Delta\tau$ the particles are randomly selected and replaced by fresh fluid particles of age 0 without considering the chemical reactions. The time evolution of the concentrations are then obtained by numerical integration of eqs 9 and 10 with Gear's method during time interval $[0, \Delta\tau]$. In the original $R_2$IEM scheme at the end of the interval $\Delta\tau$, the mean concentration is evaluated via eq 5. To further improve the accuracy of the scheme, in the present work, eq 5 is substituted into eqs 9 and 10, and the mean concentration field is evaluated simultaneously with the concentrations in all fluid particles. At the end of $\Delta\tau$, an existing particle is randomly selected and replaced by a particle of age 0 and with feed concentration. The integration is then repeated for period $[\Delta\tau, 2\Delta\tau]$, and so on.

## Results and Discussion

The bifurcation diagram for the G–S model under perfect CSTR limit is demonstrated in Figure 1.[11,31] The solid curve and the dashed curve represent the lower SN and the Hopf bifurcation curves, respectively. Within the solid (SN) curve enveloped region, three steady states coexist with the middle one unstable. Outside the enveloped region, only the washout steady state can exist. Between the lower SN and the Hopf bifurcation curves, stable limit cycle can occur when $k < 0.035$. If $k$ is larger than 0.035, an unstable limit cycle will occur.

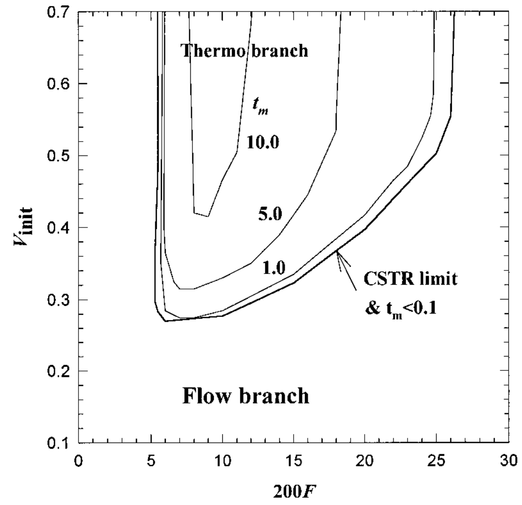

**Figure 2.** Attraction basin for thermobranches and flow branches. $U_{init} = 0.2$, $k = 0.05$.

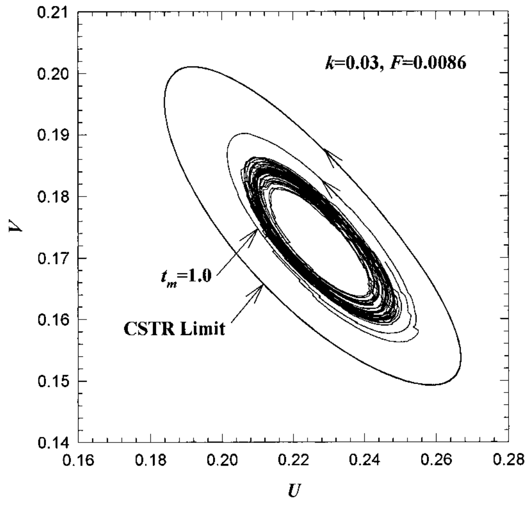

**Figure 3.** Limit cycle attractor for the Gray–Scott model under complete (CSTR limit) and incomplete micromixing ($t_m = 1.0$). $k = 0.03$, $F = 0.0086$.

**Steady-State Multiplicity.** In the bistable region, different steady states can be approached if a different initial condition is employed. Simulation results with $k = 0.05$ and $U_{init} = 0.2$ under various $t_m$ values are demonstrated in Figure 2. Notably, an incomplete micromixing will largely reduce the attraction basin of a thermodynamic steady state or thermobranch. That is, the lacking of efficient interchange of mass among particles is unfavorable to a thermobranch, and the reactants tend to wash out easily. This can be explained qualitatively by observing the reaction kinetics in eqs 9 and 10. With a feed with a concentration vector ($U_f$, $V_f$) = (1.0, 0.0), the early mixing (less $t_m$) will raise the mean concentration of $U$ and reduce the corresponding $V$. In the present work, such a disturbance in concentration vector is to decrease the increasing rate in $U$, and also the diminishing rate of $V$ owing to the product of $UV^2$, thereby preferring the thermobranch.

The results with a $t_m$ higher than 10.0 will cause the thermobranch to almost vanish, corresponding to a shrinkage of the bistable region on the $k$–$F$ plane as demonstrated in Figure 1. The data with a $t_m$ less than 0.1 will, on the other hand, almost coincide with the perfect CSTR limit in Figure 2. The applications on G–S model with a mixing time less than 0.1 can thereby be taken as well-micromixed. This is an order of magnitude less than the corresponding value for Oregonator model (1.0),[27] which reveals that the so-called "well-micromixed" limit for a tank is dependent on the chemical kinetics involved. Parallel conclusions had also been drawn in macromixing studies.[9–11]

In the literature, with a poor mixing, the thermobranch has been found to shrink ($ClO_2^-/I^-$)[36] or to expand ($BrO_3^-/Br^-/Ce^{3+}$),[37] depending on the chemical kinetics involved. The present results apparently correspond to the former case.

It is noted that close to the two limiting $F$ values forming the boundaries of the thermobranch in Figure 2 (for example, $200F = 5.9$ and 18.2 for $t_m = 5.0$), there exists some fuzziness for determining the attraction basin for thermobranches or flow branches. This is due to the random replacement nature of the incomplete micromixing, which will be discussed further in the last section.

**Relative Stability between Oscillatory and Stationary States.** When $k < 0.035$, the limit cycle attractor appears under perfect CSTR conditions. Under incomplete micromixing, limit cycle behavior can also be identified. One example is given in Figure 3. Two things are noticed. First, the size of the attractor and also the corresponding boundary of the attraction basin largely shrink as $t_m$ increases, which is similar to that with incomplete macromixing.[11] The critical $k$ value dividing the stable and unstable limit cycles regions (denoted as SLC and ULC in Figure 1) is also affected by incomplete micromixing, as indicated by the arrows in Figure 1. Such a result reveals that incomplete mixing, in either micro- or macroscales, tends to weaken the oscillatory behavior of the system. Second, the limit cycle trajectory is not unique but exhibits a random-response behavior. This is also due to the random replacement nature of the model.

Dutt and Muller[38] had reported the coexistence between the oscillatory state and the stationary steady state. They had found the limit cycle attractor expands as the mixing becomes better. This is qualitatively consistent with the findings reported in Figure 3.

**Initial-Condition Sensitive Dynamics.** Incomplete mixing might induce new dynamical behavior for nonlinear dynamic systems.[39] Gyorgyi and Field[5] had argued that the experimentally observed chaos may arise from the coupling of the nonlinear chemical kinetics and the incomplete mixing. Menzinger and Jankowski[40] had concluded from their experimental works on the Belusov–Zhabotinsky reaction that the limit cycle trajectory can be largely influenced by the so-called noise-induced transition (NIT) mechanism. The origin of their system noise is generated by external flow and the stirring, which should be contributed by both macro- and micromixing. Valent and Adamcikova[41] found in their work that the dynamical behavior in their nitrogen flow agitated bromate–thiocynate is extremely sensitive to the initial conditions. In this investigation, a new dynamical behavior that is sensitive to the initial conditions and the stochastic feed has been identified. Menzinger and Giraudi[42] reported the irregularity in amplitude and period of their oscillatory $ClO_2^- + I^-$ system, which is speculated as being due to the random perturbation of the limit cycle by discrete packets of reactants before they have been mixed into the bulk.

In Figures 4 and 5, a sensitive dependence of the initial conditions on the selection of the thermobranch (Figure 4) or the limit cycle (LC) attractor (Figure 5) or the washout state as the final state is obvious as well. It is also noted that, besides the trajectories themselves, the LC attractor and the thermobranch attractor in Figures 4 and 5 are both of a stochastic response nature. That is, the trajectory would be bound in a confined space but would never return back and reproduce itself.

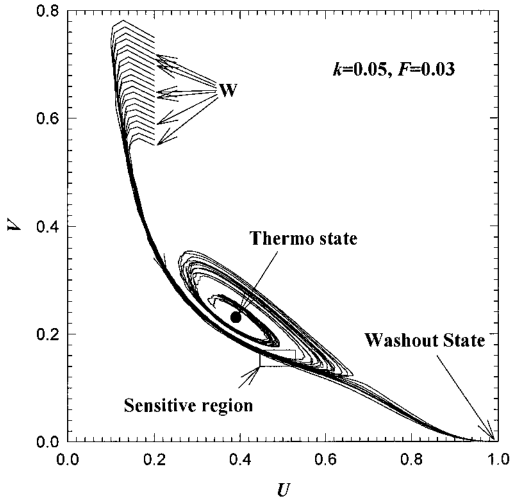

**Figure 4.** Initial-condition-sensitive response behavior between two stationary steady states. $k = 0.05$, $F = 0.03$, $t_m = 1.0$. Integration time 300. The initial conditions indicated by the symbol "W" will go to washout state and the others to the thermo steady state eventually.

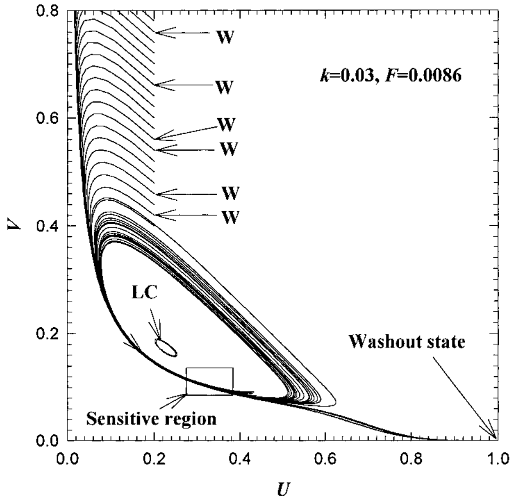

**Figure 5.** Initial-condition-sensitive response behavior between oscillatory and stationary steady states. $k = 0.03$, $F = 0.0086$, $t_m = 1.0$. Integration time 500. The initial conditions indicated by symbol "W" will go to washout state and the others to the limit cycle (LC) eventually.

We find that repeated simulations with the same parameter set (including initial conditions) cannot always reach the same final state if a different random number sequence is employed. (This can be easily achieved by using a different seed number in random number generation.) The reason corresponds to the stochastic response behavior observed is therefore the random replacement action of the IEM model. A closer look at the trajectories of the state evolution in Figures 4 and 5 shows that in spite of initial conditions under the study all states will quickly be attracted to a path with a quite narrow span, denoted as the sensitive region in the figures. Since the random replacement of particles is occurring with a relatively shorter period than the evolution time, the feed of fresh particles and the mass exchange between all other existing particles provide a continuous concentration fluctuations to the evolution state. The rectangles in Figures 4 and 5 are regions very sensitive to these fluctuations; that is, if a fresh particle is fed into the system when the state is evolving across this region, the state may be pushed to a washout state. Otherwise, the thermobranch or the LC attractor is reached.

If the initial conditions are set away from the boundary dividing the bistable and washout regions in Figure 1, the final state is little influenced by the feed particles. The corresponding trajectories form no such sensitive regions in Figures 4 and 5. The attraction basins for different steady states are definite.

Notably, Liu and Scott[43] have examined the boundary of the attraction basin of coexisting bistable states in a forced G−S model. Their model is taken under the CSTR limit; as a result, the process is deterministic in nature. Liu and Scott found that the boundary of the attraction basin would become a fractal at sufficiently high forcing amplitude, while the period-doubling bifurcation of one attractor can be identified. This is not the case for the present $R_2$IEM model, nevertheless, since the fluctuations introduced are stochastic in nature. The boundary of the attraction basin is fuzzy as well but is not reproducible when different random number sequence is employed.

The initial-condition-sensitive behavior thus observed is therefore a kind of noise-induced random response, which is interesting and may be of paractical importance since in a real, incompletely micromixed tank random concentration fluctuations exist everywhere. (Clearly, in a perfect CSTR the feed is continuous, and all concentrations are instantly leveled off which thereby provides no fluctuations.) Ruoff[22] had proposed a stochastic analysis to explain the effects of stirring on the oscillation period of the Belousov−Zhabotinsky (BZ) reaction in a closed tank. Ruoff assumed that there existed many excitable particles containing low bromide ion concentration to ignite oscillations, whose number decreases with increasing macromixing rate. If the excitable particle number is large enough (very poor macromixing), chaos can occur. Hsu et al.[10] also found complex oscillations of the BZ reaction if the macromixing is insufficient. In some sense their works can both be viewed as a kind of fluctuation-induced stochastic response as well. However, the result reported in the present paper for the first time identifies such a category of stochastic response behavior under incomplete micromixing. That is, if a system had a sensitive region for the state evolution as shown in Figures 4 and 5, it can exhibit an apparently chaotic-like behavior if a continuous fluctuation is imposed owing to incomplete micromixing.

**Role of Statistical Noises.** The random replacement concept used in the $R_2$IEM model is not new, which may be traced back to Spielman and Levenspiel,[44] who had employed a similar replacing strategy in CD modeling. Fox and Villermaux[18] had discussed the possible statistical noises introduced by the introduction scheme of fluid particles inherent to the IEM model. They claimed strongly that the proposed IEM model is superior to the traditional CD model owing to the relatively lower statistical noises since the mean concentration is evaluated by intregration and the mass transfer occurs continuously. Actually, in the IEM model the statistical noise exists as well due to the replacement action of the fluid particle. The use of random replacement scheme as employed in the $R_2$IEM model has the advantage of directly averaging over all fluid particles as the mean concentration, as employed in CD model. Such a scheme is more convenient than, and is numerically more stable than, the implicit integral of the standard IEM model. The disadvantage, however, is the greater statistical noise thus introduced.

To examine whether the so-observed dynamical behavior is the result of the greater statistical noises introduced by the $R_2$-IEM model, or of the real fluctuations among fluid particles in the physical space, a set of simulations accounting for the standard deviations from the corresponding mean concentration is conducted. The maximum standard deviations for the reactant concentration $U$ at the same initial conditions and the system parameters as in Figures 4 and 5 are approximately 0.09, 0.07, 0.06, and 0.03 when the fluid particle number is 100, 500, 1000, and 5000, respectively. The standard deviation is markedly reduced by the increase of fluid particle number; nevertheless, the basic initial-condition-sensitive dynamical features for the G−S model has remained unchanged. The amplitude of the statistical noise in the $R_2$IEM model is therefore not attributed to the observed initial-condition-sensitive dynamics, which should be induced by the interactions between fluid particles existing in the stirred tank. This conclusion applies as well to the conventional IEM model. Furthermore, the statistical noise inherent to the present $R_2$IEM model can function as an external disturbance as the heterogeneity introduced by incomplete macromixing.[42]

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