

# Fluctuating Hydrodynamics of Reactive Fluid Mixtures

**Aleksandar Donev**

*Courant Institute, New York University*

Molecular and Chemical Kinetics '15  
Berlin, Germany, Sept 9th 2015

- **Eric Vanden-Eijden**, Courant Institute, New York University
- **John Bell**, Lawrence Berkeley National Labs
- **Alejandro Garcia**, Physics, San Jose State University
- A number of postdocs and graduate students at Courant and LBL

# Chemical Reactions in Solution

- Many chemical reactions occur in a viscous solvent and are **diffusion-limited**, making a mean-field or “well-mixed” approximation inappropriate.
- Classical examples where the **Law of Mass Action** (LMA) reaction-diffusion equations **fails spectacularly** is annihilation  
 $A + B \rightarrow 0$   
But even in  $A + B \rightleftharpoons C$  there are power-law tail signatures in the dynamics even at chemical equilibrium [1].
- **Spatial fluctuations play a key role** in diffusion-limited reactions and spatial diffusion must be accounted for; this is different (in addition to) fluctuations coming from there being very few reactants of certain species.
- Primarily interested in the case when **fluctuations are weak**, i.e., lots of molecules are involved, but fluctuations still make a difference.

# Simulation Approaches

- The traditional approach to simulation of reaction-diffusion problems in this community is to solve the **Reaction-Diffusion Master Equation** (RDME), such as the next subvolume method.
  - Diffusion is modeled by a jump process instead of a continuous random walk or **fluctuating Fick's law** (see below).
  - The results depend strongly on the cell size and are thus **not grid-independent** (hard to fix!).
- At a basic level one can use **particle-based** reaction-diffusion models: Particles are modeled as spheres that diffuse as **independent Brownian walkers**.
  - In the **Smoluchowski model** particles react upon touching; simulated by the **First Passage Kinetic Monte Carlo** method (FPKMC) [2], called eGFRD in the biochemical community.
  - In the **Doi model** particles react with a certain binary reaction rate (as a Poisson process) while they overlap.  
We are developing a novel **Isotropic RDME** (IRDME) method but see also Sam Isaacson's **Convergent RDME** (CRDME).

# Diffusion in Liquids

- I will first try to convince you that a much better way to model diffusion at mesoscopic levels than jumping is **fluctuating hydrodynamics**.
- I will then try to convince you that diffusion in liquid solutions is strongly affected by **hydrodynamic interactions**.
- I will lastly show you a framework that includes **complete hydrodynamic transport** including cross-diffusion effects and fluctuations.
- But I will try to also indicate a number of problems that are unresolved.
- I will operate under the assumption that you **believe nonequilibrium statistical mechanics is a useful tool** in chemical reaction modeling, but will not try to convince you it is so, especially since I have essentially no experience in biological systems.

# Uncorrelated Brownian Walkers

- **Fluctuating hydrodynamics** is a coarse-grained description of mass, momentum and energy transport in fluids (gases and liquids).
- Consider **diffusion** of colloidal particles immersed in a viscous liquid; assume the particles are **uncorrelated Brownian walkers**.
- The positions of the  $N$  particles  $\mathbf{Q}(t) = \{\mathbf{q}_1(t), \dots, \mathbf{q}_N(t)\}$  follow the Ito SDEs

$$d\mathbf{Q} = (2\chi)^{\frac{1}{2}} d\mathcal{B}, \quad (1)$$

where  $\mathcal{B}(t)$  is a collection of independent Brownian motions.

- We are interested in describing a spatially coarse-grained **fluctuating empirical concentration field**,

$$c(\mathbf{r}, t) = \sum_{i=1}^N \delta(\mathbf{q}_i(t) - \mathbf{r}). \quad (2)$$

# Fluctuating Diffusion Equation

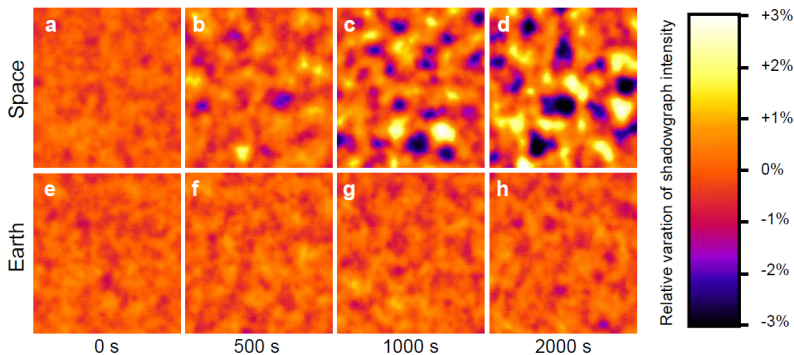
- Dean [3] obtained an SPDE for  $c(\mathbf{r}, t) = \sum \delta(\mathbf{q}_i(t) - \mathbf{r})$ , using straightforward Ito calculus and properties of the Dirac delta function,

$$\partial_t c = \chi \nabla^2 c + \nabla \cdot \left( \sqrt{2\chi c} \mathcal{W}_c \right), \quad (3)$$

where  $\mathcal{W}_c(\mathbf{r}, t)$  denotes a spatio-temporal **white-noise** vector field.

- This is a typical example of a fluctuating hydrodynamics equation, which is deceptively simple, yet extremely subtle from both a physical and mathematical perspective.
- The term  $\sqrt{2\chi c} \mathcal{W}_c$  can be thought of as a **stochastic mass flux**, in addition to the “deterministic” **Fickian flux**  $\chi \nabla c$ .
- One can develop **CFD methods** to solve this sort of SPDE [4], with lots of caveats...

# Giant Nonequilibrium Fluctuations



Experimental results by A. Vailati *et al.* from a microgravity environment [5] showing **giant fluctuations** in the concentration of polystyrene in toluene in space (box scale is 5mm on the side, 1mm thick).

**Fluctuations become macroscopically large at macroscopic scales!**

These come because of **hydrodynamic effects** on diffusion in liquids.



# Brownian Dynamics with Hydrodynamics

- The Ito equations of **Brownian Dynamics** (BD) for the (correlated) positions of the  $N$  particles  $\mathbf{Q}(t) = \{\mathbf{q}_1(t), \dots, \mathbf{q}_N(t)\}$  are

$$d\mathbf{Q} = -\mathbf{M}(\partial_{\mathbf{Q}}U) dt + (2k_B T \mathbf{M})^{\frac{1}{2}} d\mathcal{B} + k_B T (\partial_{\mathbf{Q}} \cdot \mathbf{M}) dt, \quad (4)$$

where  $\mathcal{B}(t)$  is a collection of independent Brownian motions,  $U(\mathbf{Q})$  is a conservative interaction potential.

- Here  $\mathbf{M}(\mathbf{Q}) \succeq \mathbf{0}$  is a symmetric positive semidefinite **mobility matrix** for the collection of particles, and introduces **correlations** among the walkers.
- The Fokker-Planck equation (FPE) for the probability density  $P(\mathbf{Q}, t)$  corresponding to (4) is

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial \mathbf{Q}} \cdot \left\{ \mathbf{M} \left[ \frac{\partial U}{\partial \mathbf{Q}} P + (k_B T) \frac{\partial P}{\partial \mathbf{Q}} \right] \right\}, \quad (5)$$

and is in detailed-balance (i.e., is time reversible) with respect to the **Gibbs-Boltzmann distribution**  $\sim \exp(-U(\mathbf{Q})/k_B T)$ .

# Hydrodynamic Correlations

- Let's start from the (low-density) **Rotne-Prager-Yamakawa** approximation  $\mathbf{M}_{ij} \equiv \mathbf{M}_{ij}(\mathbf{r} = \mathbf{q}_i - \mathbf{q}_j)$ , for  $r > 2\sigma$ ,

$$\mathbf{M}_{ij}(\mathbf{r}) = \frac{\mathcal{R}(\mathbf{r})}{k_B T} = \frac{\chi}{k_B T} \left[ \left( \frac{3\sigma}{4r} + \frac{\sigma^3}{2r^3} \right) \mathbf{I} + \left( \frac{3\sigma}{4r} - \frac{3\sigma^3}{2r^3} \right) \frac{\mathbf{r} \otimes \mathbf{r}}{r^2} \right]. \quad (6)$$

- Here  $\sigma$  is the radius of the colloidal particles and the **diffusion coefficient**  $\chi$  follows the Stokes-Einstein formula

$$\chi = \frac{k_B T}{6\pi\eta\sigma}.$$

- We can use Ito calculus to obtain an equation for the **empirical** or instantaneous **concentration** similar to what Dean did for uncorrelated walkers, for non-interacting particles (ideal gas,  $U = 0$ ).

# Fluctuating Fick's Law for Liquids

- We get the **stochastic advection-diffusion** equation [6]

$$\partial_t c = \nabla \cdot [\chi \nabla c] - \mathbf{w} \cdot \nabla c, \quad (7)$$

where the diffusion tensor  $\chi = \mathcal{R}(\mathbf{r}, \mathbf{r})$  and the **random velocity field**  $\mathbf{w}(\mathbf{r}, t)$  has covariance

$$\langle \mathbf{w}(\mathbf{r}, t) \otimes \mathbf{w}(\mathbf{r}', t') \rangle = 2\mathcal{R}(\mathbf{r} - \mathbf{r}') \delta(t - t'). \quad (8)$$

- For **uncorrelated walkers**,  $\mathbf{M}_{ij} = \delta_{ij} (k_B T)^{-1} \chi \mathbf{I}$ , the noise is very different,  $\nabla \cdot (\sqrt{2\chi c} \mathcal{W}_c)$ .
- In both cases the mean obeys Fick's law but the fluctuations are completely different.

The correct fluctuating Fick's law in liquids is (7) and **not** (3)!

# Fluctuating Hydrodynamics

Giant fluctuations can be modeled by including momentum transport (velocity fluctuations) in **fluctuating hydrodynamics**:

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (9)$$

$$\partial_t (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \mathbf{v}^T) + \nabla P = \nabla \cdot (\boldsymbol{\sigma} + \boldsymbol{\Sigma}) \quad (10)$$

$$\partial_t (\rho E) + \nabla \cdot (\rho E \mathbf{v} + \boldsymbol{\Pi} \cdot \mathbf{v}) = \nabla \cdot (\boldsymbol{\psi} + \boldsymbol{\Psi}) + \nabla \cdot ((\boldsymbol{\sigma} + \boldsymbol{\Sigma}) \cdot \mathbf{v}), \quad (11)$$

where the total local energy density is  $\rho E = \frac{1}{2} \rho \mathbf{v}^2 + \rho e$ .

# Momentum Fluxes

- Irreversible contribution to the stress is the viscous stress tensor

$$\boldsymbol{\sigma} = \eta (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) + \left( \zeta - \frac{2}{3} \eta \right) (\nabla \cdot \mathbf{v}) \mathbf{I} \quad (12)$$

- Stochastic stress tensor obeys fluctuation-dissipation balance**

$$\boldsymbol{\Sigma} = \sqrt{2\eta k_B T} \tilde{\boldsymbol{\mathcal{W}}} + \left( \sqrt{\frac{\zeta k_B T}{3}} - \sqrt{\frac{2\eta k_B T}{3}} \right) \text{Tr}(\tilde{\boldsymbol{\mathcal{W}}}) \mathbf{I}, \quad (13)$$

where  $\tilde{\boldsymbol{\mathcal{W}}} = (\boldsymbol{\mathcal{W}} + \boldsymbol{\mathcal{W}}^T)/\sqrt{2}$  is a symmetric white-noise tensor field.

## Chemically-Reactive Mixtures

- The species density equations for a mixture of  $N_S$  species are given by

$$\frac{\partial}{\partial t} (\rho_s) + \nabla \cdot (\rho_s \mathbf{v} + \mathbf{F}) = m_s \Omega_s, \quad (s = 1, \dots, N_S) \quad (14)$$

- The **diffusive fluxes** take the form, excluding barodiffusion and thermodiffusion, and assuming an **ideal mixture**,

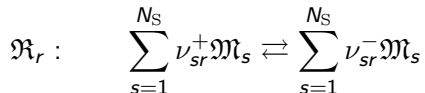
$$\mathbf{F} = \rho \mathbf{W} \left[ \chi \nabla \mathbf{x} + \sqrt{\frac{2}{n}} \chi^{\frac{1}{2}} \mathbf{W}_F(\mathbf{r}, t) \right],$$

where  $n$  is the number density,  $x_s$  is the mole fraction of species  $s$ , and  $\mathbf{W} = \text{Diag} \{w_s = \rho_s / \rho\}$  contains the mass fractions.

- $\chi$  is an **SPD diffusion tensor** that can be related to the **Maxwell-Stefan** diffusion coefficients and Green-Kubo type formulas.

# Thermodynamics of Reactions

- Consider a system with  $N_R$  **elementary reactions** with reaction  $r$



**Stoichiometric coefficients**  $\nu_{sr} = \nu_{sr}^- - \nu_{sr}^+$ , where  $\sum_s \nu_{sr} m_r = 0$ .

- Define the dimensionless **chemical affinity**

$$\mathcal{A}_r = \sum_s \nu_{sr}^+ \hat{\mu}_s - \sum_s \nu_{sr}^- \hat{\mu}_s,$$

where  $\hat{\mu}_s = m_s \mu_s / k_B T$  is the dimensionless **chemical potential per particle**.

- Also define the **thermodynamic driving force**

$$\hat{\mathcal{A}}_r = \exp \left( \sum_s \nu_{sr}^+ \hat{\mu}_s \right) - \exp \left( \sum_s \nu_{sr}^- \hat{\mu}_s \right) = \prod_s e^{\nu_{sr}^+ \hat{\mu}_s} - \prod_s e^{\nu_{sr}^- \hat{\mu}_s}$$

# Fluctuating Reaction-Diffusion

- The mass production due to chemistry can be modeled using the **Chemical Langevin Equation (CLE)** [7]:

$$\Omega_s = \sum_r \nu_{sr} \left( \frac{P}{\tau_r k_B T} \right) \hat{A}_r \text{ (deterministic LMA)} \quad (15)$$

$$+ \sum_r \nu_{sr} \left( \frac{P}{\tau_r k_B T} \prod_s e^{\nu_{sr}^+ \hat{\mu}_s} \right)^{\frac{1}{2}} \mathbf{Z}(\mathbf{r}, t) \text{ (CLE)}$$

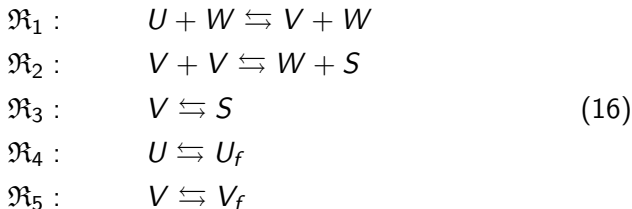
- The **CLE** follows from a truncation of the Kramers-Moyal expansion at second order. No true thermodynamic equilibrium:
  - Assumes **one-way reactions** which violates detailed balance.
  - the equilibrium distribution is not the Einstein distribution  $\exp(S/k_B)$ .
- There is no S(P)DE** that can correctly describe both the short-time (central limit theorem) and long-time (large deviation functional) behavior of the master equation. But **tau leaping** can and should be used with time splitting.



# Nonlinear Chemical Networks

We have studied the Baras-Pearson-Mansour (BPM) model

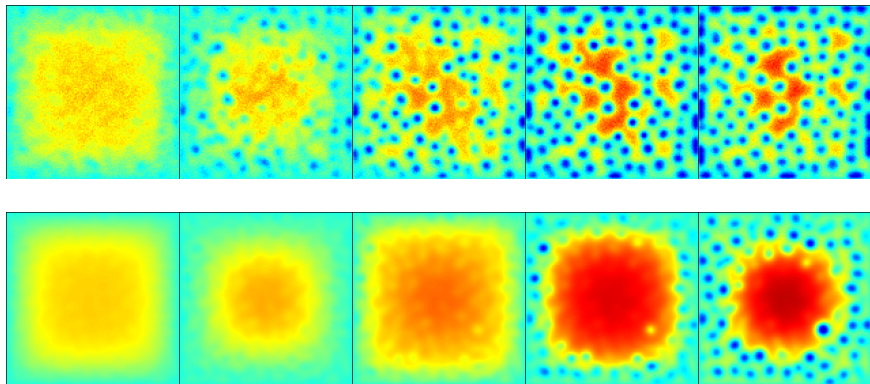
$$\mathfrak{M} = (U, V, W, S, U_f, V_f),$$



This system can exhibit **limit cycles**, bimodal states (**bistability**), and possibly other nonlinear behavior.

In principle this system can be simulated using **particle methods!**

## Turing-like Patterns



Development of an instability in the BPM model with fluctuations (top) and without (bottom) with complete compressible hydrodynamics (not just reaction-diffusion).

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