

Fluctuating hydrodynamics of reactive electrolyte mixtures

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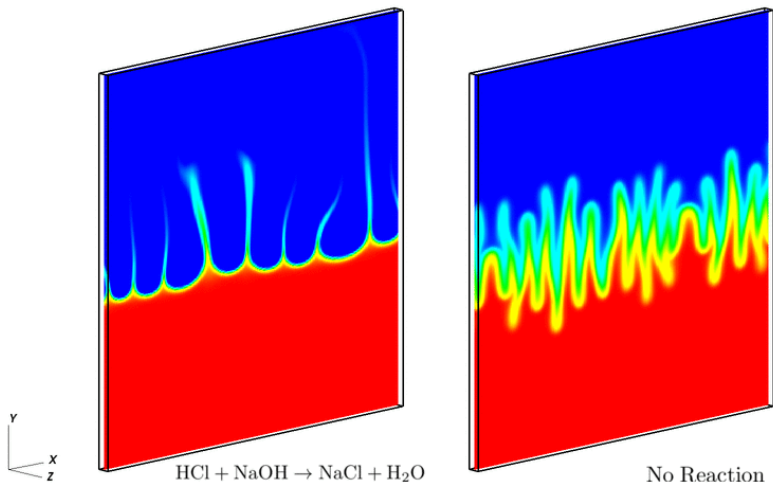
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Chemical Reactions in Solution

- **Spatial fluctuations play a key role in diffusion-limited reactive liquid mixtures.**
- Primarily interested in the case when **fluctuations are weak**, i.e., lots of molecules are involved, but fluctuations still make a difference: **fluctuating hydrodynamics (FHD)**.
- **Electrolyte solutions** are important for batteries, ion-selective membranes, biology, etc.
- As a motivating example, consider the **reaction+diffusion+gravity instability** when (0.4mol/L) NaOH is placed on top of (1mol/L) of HCl in a Hele-Shaw cell.

Acid-Base Neutralization (HCl)



Momentum fluctuations trigger the instability (GIF) [1].

Chemically-Reactive Mixtures

- The the total mass density $\rho = \sum_s \rho_s$ and the density $\rho_s = w_s \rho$ of species s for a mixture of N_S species satisfy

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

$$\frac{\partial}{\partial t} \rho + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (2)$$

- The **dissipative and stochastic diffusive mass fluxes** are

$$\mathbf{F}_d = \rho \mathbf{W} \left[\chi \Gamma \nabla \mathbf{x} + \sqrt{\frac{2}{n}} \chi^{\frac{1}{2}} \mathcal{Z}^{\text{mass}} \right],$$

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

- We use $\mathcal{Z}(\mathbf{r}, t)$ to denote a white-noise Gaussian random field.

Fluctuation-dissipation balance condition is $\chi^{\frac{1}{2}} (\chi^{\frac{1}{2}})^T = \chi$.

- Γ is a matrix of thermodynamic factors,

$$\Gamma = \mathbf{I} + (\mathbf{X} - \mathbf{x}\mathbf{x}^T) \left(\frac{\partial^2 g_{\text{ex}}}{\partial \mathbf{x}^2} \right),$$

where $g_{\text{ex}}(\mathbf{x}, T, P)$ is the **excess Gibbs energy density** per particle.

- χ is an **SPD diffusion tensor** that can be related to the Maxwell-Stefan diffusion coefficients.
- **We do not know** values of these as a function of composition for even a single ternary mixture!

We have studied **ideal mixtures**: hard-sphere **gas mixtures** [2] and **dilute solutions** [3, 4, 1].

Mixture Model

- We consider constant temperature and pressure and focus on compositional-dependence of **chemical potentials**

$$\mu_s(\mathbf{x}, T, P) = \mu_s^0(T, P) + \frac{k_B T}{m_s} \log(x_s \gamma_s), \quad (3)$$

where $\gamma_s(\mathbf{x}, T, P)$ is the activity ($\gamma_s = 1$ for **ideal mixtures**).

- Here we restrict thermodynamics to focus on **entropy of mixing** and assume the **Boussinesq equation of state (EOS)**:

$$\rho(\mathbf{w}, T, P) = \rho_0 = \text{const.}$$

- More general EOS in **low Mach number models** challenging with reactions:

$$\sum_{i=1}^N \frac{\rho_i}{\bar{\rho}_i} = \rho \sum_{i=1}^N \frac{w_i}{\bar{\rho}_i} = 1.$$

Momentum Equation

- Fluid velocity \mathbf{v} and mechanical component of the pressure π :

$$\partial_t(\rho\mathbf{v}) + \nabla\pi = -\nabla \cdot (\rho\mathbf{v}\mathbf{v}^T) + \nabla \cdot (\eta\bar{\nabla}\mathbf{v} + \boldsymbol{\Sigma}) + \rho_{\text{true}}(\mathbf{w})\mathbf{g}$$

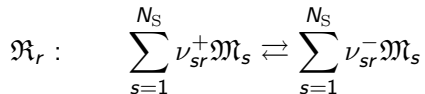
$$\nabla \cdot \mathbf{v} = -\nabla \cdot \left(\sum_{i=1}^N \frac{\mathbf{F}_i}{\bar{\rho}_i} \right) = 0 \text{ for Boussinesq,}$$

- **Stochastic momentum flux** from FHD:

$$\boldsymbol{\Sigma} = \sqrt{\eta k_B T} [\mathcal{Z}^{\text{mom}} + (\mathcal{Z}^{\text{mom}})^T]. \quad (4)$$

Thermodynamics of Reactions

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



with **stoichiometric coefficients** $\Delta\nu_{sr}^+ = \nu_{sr}^- - \nu_{sr}^+ = -\Delta\nu_{sr}^-$.

- The thermodynamic driving force for reactions is a **nonlinear chemical affinity**, giving the nonlinear **reaction propensities**

$$a_r^\pm = \lambda_r \prod_s e^{\nu_{sr}^\pm \hat{\mu}_s} = \kappa_r^\pm \prod_s (x_s \gamma_s)^{\nu_{sr}^\pm}. \quad (5)$$

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

- The equilibrium constant is a purely thermodynamic quantity,

$$K_r(T, P) = \frac{\kappa_r^+}{\kappa_r^-} = \exp \left(- \sum_s \Delta\nu_{sr}^+ \hat{\mu}_s^0 \right). \quad (6)$$

Fluctuations in Chemical Reactions

- A Gaussian FHD model: **Chemical Langevin Equation** (CLE) [2, 4]:

$$\Omega_s^{\text{CLE}} = \sum_r \sum_{\alpha=\pm} \Delta \nu_{sr}^{\alpha} (a_r^{\alpha} + \sqrt{a_r^{\alpha}} \mathcal{Z}_r^{\text{react}}), \quad (7)$$

- **CLE is inconsistent with statistical mechanics:**
The equilibrium distribution is *not* the Einstein distribution.
- **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 chemical master equation.
- FHD is a mesoscopic model that requires spatial discretization into **well-mixed coarse-graining cells** of volume ΔV .

Chemical Master Equation

- The **chemical master equation (CME)** for the number of molecules N_s of species s in a given cell is

$$dN_s = \Omega_s \Delta V = \sum_r \sum_{\alpha=\pm} \Delta \nu_{sr}^{\alpha} \mathcal{P}(a_r^{\alpha} \Delta V dt), \quad (8)$$

where $\mathcal{P}(m)$ denotes a Poisson random variables with mean m .

- The noise here is **Poisson and not Gaussian** and this matters for large deviation theory.
- **Tau leaping** instead of Euler-Maruyama (just replace Gaussian random numbers with Poisson ones!):

$$N_s(t + \Delta t) - N_s(t) = \sum_r \sum_{\alpha=\pm} \Delta \nu_{sr}^{\alpha} \mathcal{P}(a_r^{\alpha} \Delta V \Delta t).$$

Dimerization Reaction

- **Dimerization reaction** in a binary mixture in a single cell,



$$N_1 \text{ (monomers)} + 2N_2 \text{ (dimers)} = \rho_0 \Delta V / m \equiv N_0 \quad (10)$$

- **Entropy of mixing** dominates the entropy

$$S(N_1, N_2) = k_B \log \frac{(N_1 + N_2)!}{N_1! N_2!} - k_B (N_1 \hat{\mu}_1^0 + N_2 \hat{\mu}_2^0). \quad (11)$$

- Obtaining the **Einstein equilibrium distribution**

$$P_{\text{eq}}(N_2) \sim e^{S(N_0 - 2N_2, N_2)/k_B} \rightarrow \exp[-k_B N \sum_s x_s \log(x_s/x_s^{\text{eq}})] \quad (12)$$

requires the **detailed balance condition**

$$a^+(N_2) \equiv \kappa^+ \left(\frac{N_1}{N_1 + N_2} \right) \left(\frac{N_1 - 1}{N_1 + N_2 - 1} \right) \rightarrow \kappa^+ x_1^2, \quad (13)$$

$$a^-(N_2) \equiv \kappa^- \left(\frac{N_2}{N_1 + N_2} \right) \rightarrow \kappa^- x_2. \quad (14)$$

Numerical Results

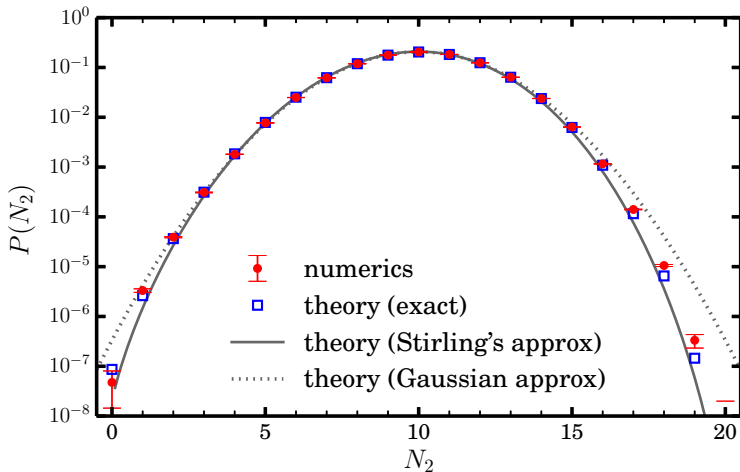


Figure: Equilibrium distribution for a dimerization reaction.

- When some species are charged we have **electrodiffusion** (z_s is charge per mass) [5]:

$$\mathbf{F} = \mathbf{F}_d - \frac{\rho^2}{nk_B T} (\mathbf{W}\chi\mathbf{W}z) \nabla\phi.$$

- A key mesoscopic length is the **Debye length**

$$\lambda_D \approx \left(\frac{\epsilon k_B T}{\sum_{k=1}^N \rho w_k m_k z_k^2} \right)^{1/2}. \quad (15)$$

- At scales comparable to λ_D we have the Poisson equation

$$-\nabla \cdot (\epsilon \nabla \phi) = q^f = \sum \rho_s z_s.$$

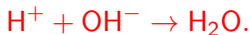
- We have shown that [6, 5] **fluctuating electrohydrodynamics reproduces all the results of Onsager-Debye-Huckel theory.**

Electroneutral Limit

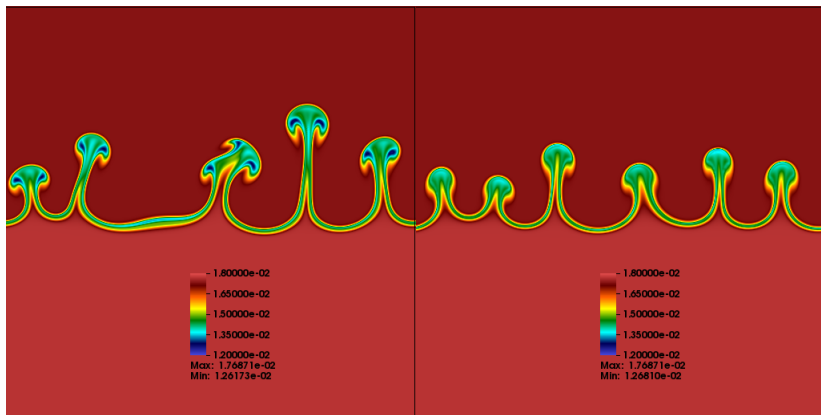
- At scales much larger than λ_D the fluid is charge-free, $q_f \rightarrow 0$, and we have the **electroneutral limit**

$$\nabla \cdot \left[\frac{\rho^2}{nk_B T} (\mathbf{z}^T \mathbf{W} \chi \mathbf{W} \mathbf{z}) \nabla \phi \right] = \nabla \cdot (\mathbf{z}^T \mathbf{F}_d).$$

- **Boundary conditions** are complicated and in general not known except for binary electrolytes.
- Modeling electrodiffusion of ions **requires solving a Poisson equation** and is different from diffusion of neutral molecules, even at scales much larger than Debye length!
- Going back to the acid-base example, **all species are ions** (H^+ , Na^+ , Cl^- and OH^-) and the reaction is



Acid-Base Neutralization (HCl)



Ions (left) versus molecules (right) (MP4)

- How to account for dependence of density on composition without introducing compressibility (sound waves): low Mach models? Will barodiffusion make a comeback?
- Do fluctuations influence instabilities in “real life” and how?
- What is the spatial resolution limit of fluctuating hydrodynamics?
- How to go beyond FHD at near-molecular scales: modeling ions as particles?

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