Fluctuating hydrodynamics of complex fluid flows

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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 $\mathbf{Q}(t) = \{\mathbf{q}_1(t), \ldots, \mathbf{q}_N(t)\}$ follow the Ito SDEs

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

  where $\boldsymbol{\mathcal{B}}(t)$ is a collection of independent Brownian motions.
- We are interested in describing a spatially coarse-grained **fluctuating empirical concentration field**,

$$c_\xi(\mathbf{r}, t) = \sum_{i=1}^{N} \delta_\xi(\mathbf{q}_i(t) - \mathbf{r}), \tag{2}$$

  where δ_ξ is a smoothing kernel with support $\sim \xi$ that converges to a delta function as $\xi \to 0$.

No Coarse Graining ala Dean

- Consider first the limit $\xi \to 0$, which corresponds to **no coarse graining** (no loss of information except particle numbering).
- Dean 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,

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

  where $\boldsymbol{\mathcal{W}}_c(\mathbf{r}, t)$ denotes a spatio-temporal **white-noise** vector field.
- This is a typical example of a fluctuating hydrodynamics equation, which is deceptively simply, yet extremely subtle from both a physical and mathematical perspective.
- The term $\sqrt{2\chi c}\, \boldsymbol{\mathcal{W}}_c$ can be thought of as a **stochastic mass flux**, in addition to the "deterministic" **Fickian flux** $\chi \boldsymbol{\nabla} c$.

What is it useful for?

$$\partial_t c = \chi \boldsymbol{\nabla}^2 c + \boldsymbol{\nabla} \cdot \left(\sqrt{2\chi c}\, \boldsymbol{\mathcal{W}}_c \right) \tag{4}$$

- In principle, the Dean equation is **not really useful**, since it is a **mathematically ill-defined** tautology, a mere rewriting of the original equations for the particles.
- The ensemble average $\bar{c} = \langle c \rangle$ follows **Fick's law**,

$$\partial_t \bar{c} = \boldsymbol{\nabla} \cdot (\chi \boldsymbol{\nabla} \bar{c}) = \chi \boldsymbol{\nabla}^2 \bar{c},$$

  which is the **law of large numbers** (most probable path around which all paths concentrate) in the limit of **large coarse-graining scale** ξ.
- The **central limit theorem** describing small Gaussian fluctuations $\delta c = c - \bar{c}$ can be obtained by linearizing,

$$\partial_t (\delta c) = \chi \boldsymbol{\nabla}^2 (\delta c) + \boldsymbol{\nabla} \cdot \left(\sqrt{2\chi \bar{c}}\, \boldsymbol{\mathcal{W}}_c \right).$$

  Note that this equation of **linearized fluctuating hydrodynamics** is mathematically **well-defined**.

What is it useful for?

- Furthermore, and more surprisingly, the Dean equation correctly predicts the **large deviation** action functional for the particle model, and thus correctly gives the probability of observing large deviations from the typical (Fick) behavior.
- This suggests the nonlinear fluct. hydro. equation is **informative and maybe useful**.
- In particular, upon **spatially discretizing** the (formal) SPDE, the resulting system of SODEs can be seen as a spatial coarse-graining of the particle system, which has the right properties.
- **Numerically solving** the discretized Dean equation with **weak noise** gives results in agreement with **all three** mathematically well-defined weak-noise limit theorems: LLN, CLT, and LDT.
  No need to perform linearizations manually, or to discretize stochastic path integrals directly.

Brownian Dynamics

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

$$d\mathbf{Q} = -\mathbf{M}(\partial_{\mathbf{Q}} U)\, dt + (2k_B T\, \mathbf{M})^{\frac{1}{2}}\, d\boldsymbol{\mathcal{B}} + k_B T\, (\partial_{\mathbf{Q}} \cdot \mathbf{M})\, dt, \qquad (5)$$

  where $\boldsymbol{\mathcal{B}}(t)$ 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** block **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 (5) is

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial \mathbf{Q}} \cdot \left\{ \mathbf{M} \left[\frac{\partial U}{\partial \mathbf{Q}} P + (k_B T) \frac{\partial P}{\partial \mathbf{Q}} \right] \right\}, \qquad (6)$$

  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) **pairwise approximation**

$$\forall (i,j): \quad \mathbf{M}_{ij}(\mathbf{q}_i, \mathbf{q}_j) = \frac{\mathcal{R}(\mathbf{q}_i, \mathbf{q}_j)}{k_B T} = \frac{1}{k_B T} \sum_k \phi_k(\mathbf{q}_i) \phi_k(\mathbf{q}_j),$$

- Here $\mathcal{R}(\mathbf{r}, \mathbf{r}')$ is a **symmetric positive-definite kernel** that is **divergence-free**, and can be diagonalized in an (infinite dimensional) set of divergence-free basis functions $\phi_k(\mathbf{r})$.
- For the **Rotne-Prager-Yamakawa tensor** mobility, $\mathcal{R}(\mathbf{r}', \mathbf{r}'') \equiv \mathcal{R}(\mathbf{r}' - \mathbf{r}'' \equiv \mathbf{r})$,

$$\mathcal{R}(\mathbf{r}) = \chi \begin{cases} \left(\frac{3\sigma}{4r} + \frac{\sigma^3}{2r^3}\right)\mathbf{I} + \left(\frac{3\sigma}{4r} - \frac{3\sigma^3}{2r^3}\right)\frac{\mathbf{r}\otimes\mathbf{r}}{r^2}, & r > 2\sigma \\ \left(1 - \frac{9r}{32\sigma}\right)\mathbf{I} + \left(\frac{3r}{32\sigma}\right)\frac{\mathbf{r}\otimes\mathbf{r}}{r^2}, & r \le 2\sigma \end{cases} \tag{7}$$

where σ is the radius of the colloidal particles and the **diffusion coefficient** χ follows the Stokes-Einstein formula $\chi = k_B T / (6\pi\eta\sigma)$.

Eulerian Overdamped Dynamics

- We can use standard calculus to obtain an equation for the **empirical** or instantaneous **concentration**

$$c(\mathbf{r},t)=\sum_{i=1}^{N}\delta\left(\mathbf{q}_i(t)-\mathbf{r}\right). \tag{8}$$

- Following a similar procedure to Dean now, we get the **stochastic advection diffusion** equation [1]

$$\partial_t c=\boldsymbol{\nabla}\cdot\left[\boldsymbol{\chi}(\mathbf{r})\,\boldsymbol{\nabla}c\right]-\mathbf{w}\cdot\boldsymbol{\nabla}c, \tag{9}$$

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

$$\left\langle \mathbf{w}(\mathbf{r},t)\otimes\mathbf{w}\left(\mathbf{r}',t'\right)\right\rangle=2\boldsymbol{\mathcal{R}}\left(\mathbf{r},\mathbf{r}'\right)\delta\left(t-t'\right). \tag{10}$$

- This equation is now well-defined mathematically since linear. One can use the same equation (9) to evolve a probability distribution for finding a particle at a given location.

Importance of Hydrodynamics

- For **uncorrelated walkers**, $\mathbf{M}_{ij} = \delta_{ij} \left(k_B T\right)^{-1} \chi \mathbf{I}$, the noise is very different, $\boldsymbol{\nabla} \cdot \left(\sqrt{2\chi c}\, \boldsymbol{\mathcal{W}}_c\right)$.
- In both cases (hydrodynamically correlated and uncorrelated walkers) the mean obeys Fick's law but the fluctuations are completely different.
- For uncorrelated walkers, out of equilibrium the fluctuations develop very weak long-ranged correlations.
- For hydrodynamically correlated walkers, **out of equilibrium** the fluctuations exhibit very strong **"giant" fluctuations** with a power-law spectrum truncated only by gravity or finite-size effects. These giant fluctuations have been **confirmed experimentally**.

Particle Interactions

$$U(\mathbf{Q}) = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} U_2(\mathbf{q}_i, \mathbf{q}_j) \tag{11}$$

- Cranking the crank yields the not-so-useful "DDFT" equation

$$\partial_t c(\mathbf{r}, t) = -\boldsymbol{\nabla} \cdot (\mathbf{w}(\mathbf{r}, t)\, c(\mathbf{r}, t)) + \boldsymbol{\nabla} \cdot (\chi(\mathbf{r}) \boldsymbol{\nabla} c(\mathbf{r}, t))$$
$$+ (k_B T)^{-1} \boldsymbol{\nabla} \cdot \left(c(\mathbf{r}, t) \int \mathcal{R}(\mathbf{r}, \mathbf{r}') \boldsymbol{\nabla}' U_2(\mathbf{r}', \mathbf{r}'') c(\mathbf{r}', t) c(\mathbf{r}'', t)\, d\mathbf{r}' d\mathbf{r}'' \right).$$

- All of the equations of fluctuating hydrodynamics have the same structure of a generic Langevin equation, including these ones:

$$\partial_t c = -\boldsymbol{\mathcal{M}}[c(\cdot, t)] \frac{\delta H}{\delta c(\cdot, t)} + (2 k_B T \boldsymbol{\mathcal{M}}[c(\cdot, t)])^{\frac{1}{2}} \diamond \boldsymbol{\mathcal{W}}(\cdot, t)$$

Generic Structure of Langevin Equations

- Here the **coarse-grained Hamiltonian** is independent of the dynamics,

$$H\left[c\left(\cdot\right)\right] = k_B T \int c\left(\mathbf{r}\right)\left(\ln\left(\Lambda^3 c\left(\mathbf{r}\right)\right) - 1\right)\, d\mathbf{r} + \frac{1}{2}\int U_2(\mathbf{r},\mathbf{r}')c(\mathbf{r})c(\mathbf{r}')\, d\mathbf{r}d\mathbf{r}'$$

- But the mobility operator depends on dynamics

$$\left(\boldsymbol{\mathcal{M}}\, f\left(\cdot\right)\right)\left(\mathbf{r}\right) = \int d\mathbf{r}'\mathcal{M}\left[c(\cdot);\, \mathbf{r},\mathbf{r}'\right]\, f(\mathbf{r}') =$$

$$\equiv \begin{cases} -\left(k_B T\right)^{-1}\, \boldsymbol{\nabla}\cdot\left(\chi(\mathbf{r})c(\mathbf{r})\boldsymbol{\nabla} f(\mathbf{r})\right) & \text{no hydro} \\ -\left(k_B T\right)^{-1}\, \boldsymbol{\nabla}\cdot\left(c(\mathbf{r})\int \boldsymbol{\mathcal{R}}\left(\mathbf{r},\mathbf{r}'\right) c(\mathbf{r}')\boldsymbol{\nabla}' f(\mathbf{r}')\, d\mathbf{r}'\right) & \text{hydro} \end{cases}$$

Fluctuating Hydrodynamics

- The thermal velocity fluctuations are described by the (unsteady) **fluctuating Stokes equation**,

$$\rho\partial_t \mathbf{v} + \boldsymbol{\nabla}\pi = \eta\boldsymbol{\nabla}^2\mathbf{v} + \sqrt{2\eta k_B T}\,\boldsymbol{\nabla}\cdot\boldsymbol{\mathcal{W}}, \quad \text{and } \boldsymbol{\nabla}\cdot\mathbf{v} = 0. \tag{12}$$

  where the **stochastic momentum flux** is spatio-temporal **white noise**,

$$\langle \mathcal{W}_{ij}(\mathbf{r},t)\mathcal{W}^{\star}_{kl}(\mathbf{r}',t')\rangle = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\,\delta(t-t')\delta(\mathbf{r}-\mathbf{r}').$$

  The solution of this SPDE is a white-in-space distribution (very far from smooth!).

- Define a **smooth advection velocity** field, $\boldsymbol{\nabla}\cdot\mathbf{u} = 0$,

$$\mathbf{u}(\mathbf{r},t) = \int \boldsymbol{\sigma}(\mathbf{r},\mathbf{r}')\,\mathbf{v}(\mathbf{r}',t)\,d\mathbf{r}' \equiv \boldsymbol{\sigma}\star\mathbf{v},$$

  where the smoothing kernel $\boldsymbol{\sigma}$ filters out features at scales below a **cutoff scale** σ.

Reversible Diffusion via Advection

- **Lagrangian** description of a **passive tracer** diffusing in the fluid,

$$\dot{\mathbf{q}} = \mathbf{u}(\mathbf{q}, t). \tag{13}$$

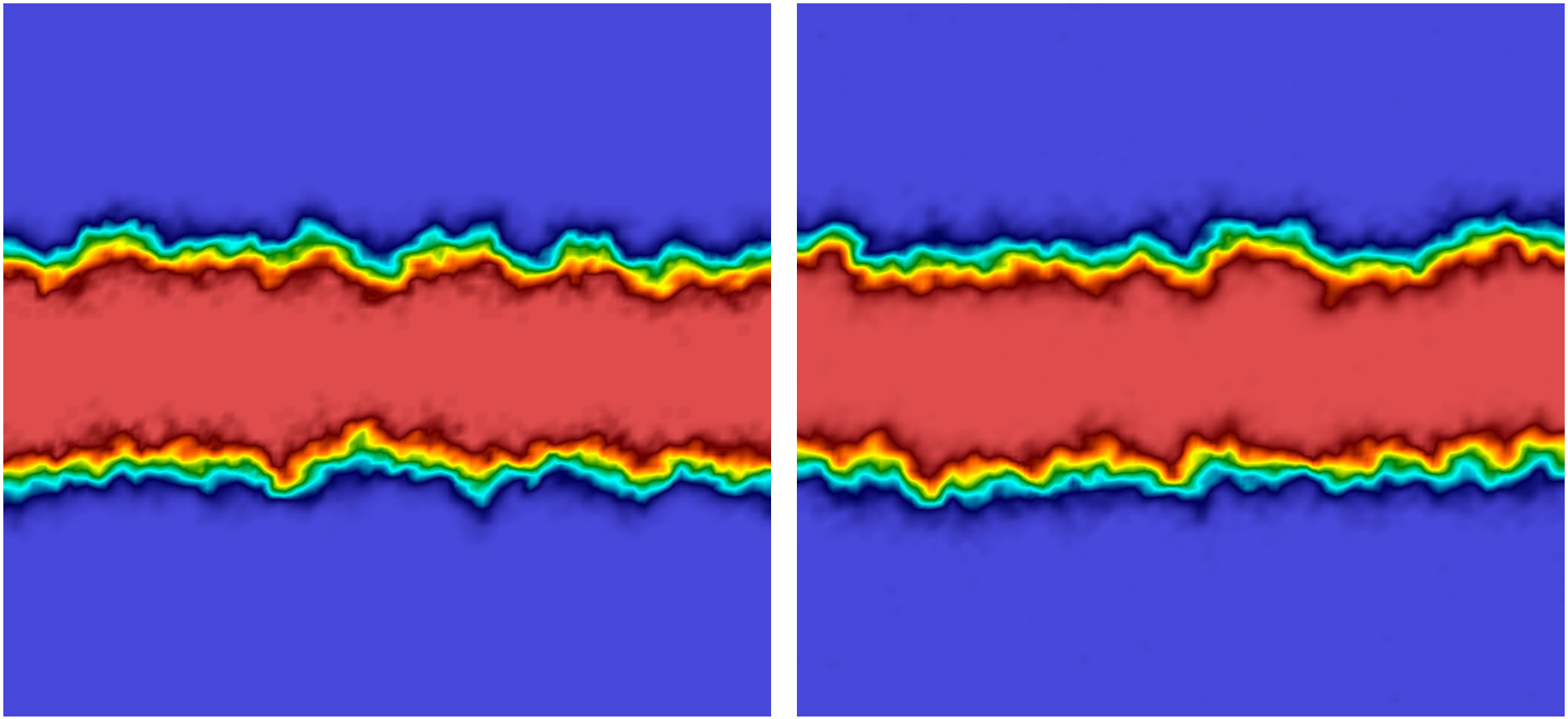
- **Eulerian** description of the **concentration** $c(\mathbf{r}, t)$ with an (additive noise) fluctuating advection-diffusion equation,

$$\partial_t c = -\mathbf{u} \cdot \boldsymbol{\nabla} c. \tag{14}$$

- The two descriptions are **equivalent**.
  $c(\mathbf{q}(t), t) = c(\mathbf{q}(0), 0)$ or, due to reversibility,
  $c(\mathbf{q}(0), t) = c(\mathbf{q}(t), 0)$.
- One can add additional **bare diffusion** χ_0 in addition to the advection,

$$\partial_t c = -\mathbf{u} \cdot \boldsymbol{\nabla} c + \chi_0 \boldsymbol{\nabla}^2 c.$$

Giant Fluctuations in Diffusive Mixing



Snapshots of concentration in a miscible mixture showing the development of a *rough* diffusive interface due to the effect of **thermal fluctuations**. These **giant fluctuations** have been studied experimentally and with hard-disk molecular dynamics [2].

Separation of Time Scales

- In liquids molecules are caged (trapped) for long periods of time as they collide with neighbors:
  Momentum and heat diffuse much faster than does mass.
- This means that $\chi \ll \nu$, leading to a **Schmidt number**

$$S_c = \frac{\nu}{\chi} \sim 10^3 - 10^4.$$

  This **extreme stiffness** solving the concentration/tracer equation numerically challenging.
- There exists a **limiting (overdamped) dynamics** for c in the limit $S_c \to \infty$ in the scaling

$$\chi\nu = \text{const.}$$

Overdamped Dynamics

- Adiabatic mode elimination gives the following limiting Ito **stochastic advection-diffusion equation** [3],

$$\partial_t c = \boldsymbol{\nabla} \cdot [\boldsymbol{\chi}(\mathbf{r}) \boldsymbol{\nabla} c] - \mathbf{w} \cdot \boldsymbol{\nabla} c, \tag{15}$$

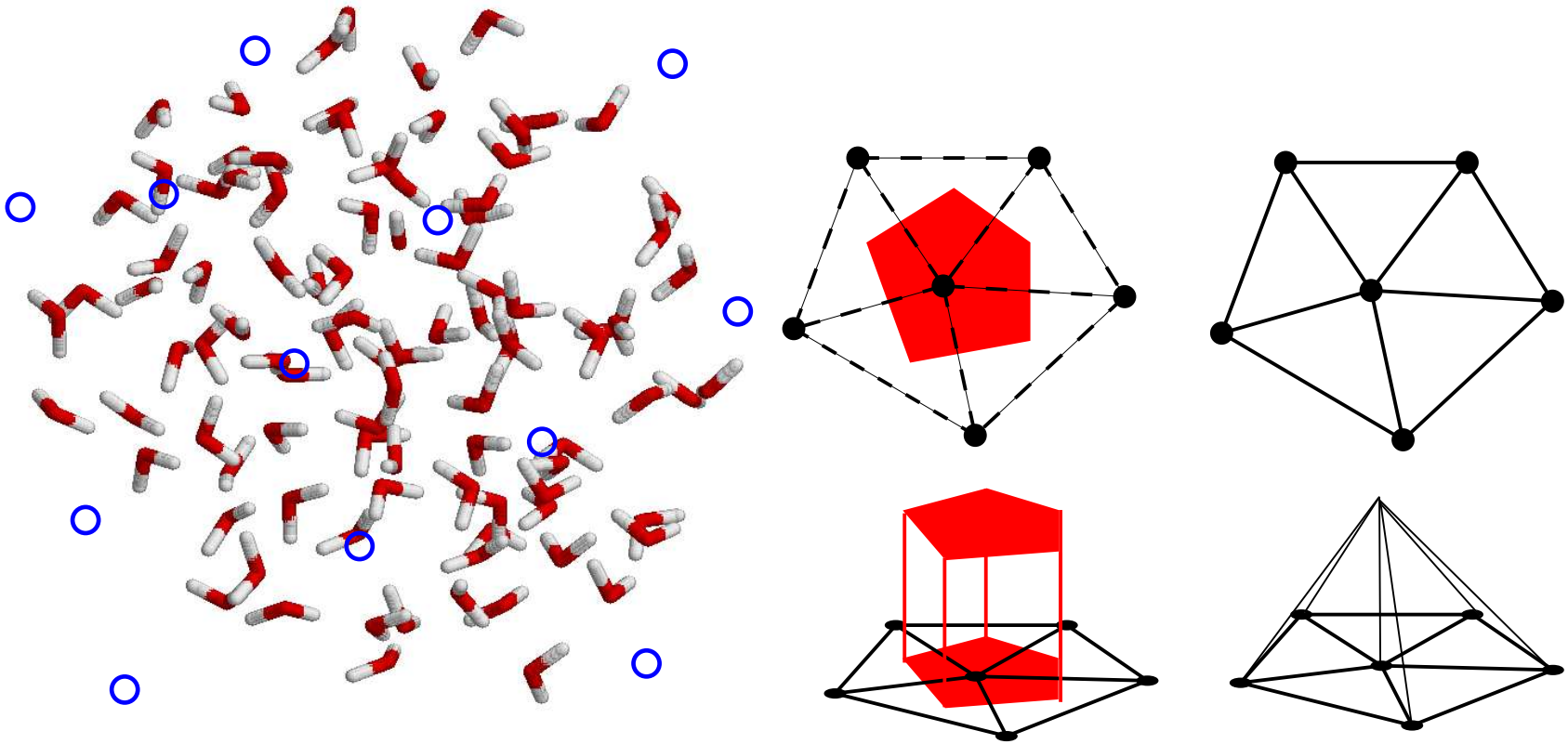
  which is **exactly the same as** what was derived from **Brownian dynamics** before.
- The advection velocity $\mathbf{w}(\mathbf{r}, t)$ is **white in time**, with covariance proportional to a Green-Kubo integral of the velocity auto-correlation function,

$$\begin{aligned}\langle \mathbf{w}(\mathbf{r}, t) \otimes \mathbf{w}(\mathbf{r}', t') \rangle &= 2\,\delta(t - t') \int_0^\infty \langle \mathbf{u}(\mathbf{r}, t) \otimes \mathbf{u}(\mathbf{r}', t + t') \rangle dt' \\ &= 2\boldsymbol{\mathcal{R}}(\mathbf{r}, \mathbf{r}')\,\delta(t - t') \\ &= \frac{k_B T}{\eta} \int \boldsymbol{\sigma}(\mathbf{r}, \mathbf{q}')\, \mathbf{G}(\mathbf{r}', \mathbf{r}'')\, \boldsymbol{\sigma}^T(\mathbf{r}'', \mathbf{q}'')\, d\mathbf{q}' d\mathbf{q}'',\end{aligned}$$

  where $\mathbf{G}$ is the Green's function for steady Stokes flow with the appropriate boundary conditions.

Coarse Graining

- The proper way to interpret fluctuating hydrodynamics is via the **theory of coarse-graining** (here I follow Pep Espanol).
- The first step is to define a discrete set of **relevant variables**, which are **mesoscopic observables**.



Relevant Variables

- How to assign the molecules to the **coarse-grained nodes**?
- If one uses a nearest-node assignment, i.e., **Voronoi cells**, one gets divergent Green-Kubo transport coefficients.
- Instead, one can use the dual **Delaunay cells** to construct coarse-grained variables [4], related to a **finite-element discretization** of the fluctuating hydrodynamic SPDE.

$$c_\mu(\mathbf{Q}) = \sum_i^N \delta_\mu(\mathbf{q}_i) = \sum_i^N \frac{\phi_\mu(\mathbf{q}_i)}{\mathcal{V}_\mu},$$

  which follow a **conservation law** since $\sum_\mu \mathcal{V}_\mu c_\mu = N$.
- The key assumption is **infinite separation of timescales**: $c_\mu(\mathbf{Q})$ is much slower than $\mathbf{Q}$ itself.

Mori-Zwanzig Formalism

- One can use the **Mori-Zwanzig formalism** with a **Markovian assumption** (due to separation of timescales) to derive a system of SDEs for the (discrete) coarse-grained variable $\mathbf{c}(\mathbf{Q})$:

$$\frac{d\mathbf{c}}{dt} = -\mathbf{M}(\mathbf{c}) \cdot \frac{\partial F(\mathbf{c})}{\partial \mathbf{c}} + (2k_B T\, \mathbf{M}(\mathbf{c}))^{\frac{1}{2}}\, \mathcal{W}(t) + (k_B T)\, \frac{\partial}{\partial c} \cdot \mathbf{M}(\mathbf{c}),$$

  with the **fluctuation-dissipation balance** $\mathbf{M}^{\frac{1}{2}} \left(\mathbf{M}^{\frac{1}{2}}\right)^{\star} = \mathbf{M}$.

- Here $F(\mathbf{c})$ is the **coarse-grained free energy**

$$P^{\mathrm{eq}}(\tilde{\mathbf{c}}) = \int d\mathbf{Q}\; \rho^{\mathrm{eq}}(\mathbf{Q}) \delta(\tilde{\mathbf{c}} - \mathbf{c}(\mathbf{Q})) \propto \exp\left\{-\frac{F(\tilde{\mathbf{c}})}{k_B T}\right\},$$

  which is a purely **equilibrium** quantity.

- The dynamics is captured by the **diffusion or mobility** SPD matrix $\mathbf{M}(\mathbf{c})$, for which one can write generalized **Green-Kubo** formulas.

Renormalization

- If one does this for diffusion-type problems one obtains something that looks very much like a **finite-element discretization** of the fluctuating hydrodynamic (formal) SPDE.
  The **SPDE is a useful notation** to guide the construction of spatio-temporal discretizations, drawing from years of CFD experience.
- However, if coarse-graining scale becomes **macroscopic**, we get **Fick's law** in the usual local form but with **renormalized free energy and transport coefficients**:

$$\partial_t c = \chi \boldsymbol{\nabla}^2 \Pi(c) = \chi \boldsymbol{\nabla} \cdot \left(\frac{d\Pi(c)}{dc} \boldsymbol{\nabla} c \right),$$

  where $\Pi(c) = c\,(df/dc) - f$ is the osmotic pressure, where $f(c)$ is the thermodynamic **thermodynamic equilibrium** free-energy.
- In-between the microscopic and macroscopic lies a whole continuum of scales: **The free energy and transport coefficients (mobility) must depend on the coarse-graining scale in nonlinear fluctuating hydrodynamics (but not in linearized fluct. hydro).**

Multiphase Systems: Liquid-Vapor

- We will use a **diffusive-interface model** for describing interfaces between two distinct phases such as liquid and vapor of a single species.
- Coarse-grained free energy follows the usual **square-gradient surface tension model**

$$F\left(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), T(\mathbf{r})\right) = \int \mathrm{d}\mathbf{r}\, \left(f\left(\rho(\mathbf{r}), T(\mathbf{r})\right) + \frac{1}{2}\kappa \left|\nabla\rho(\mathbf{r})\right|^2 \right) \quad (16)$$

  The **local free energy density** $f\left(\rho(\mathbf{r}), T(\mathbf{r})\right)$ includes the hard-core repulsions as well as the short-range attractions.
- Assume a **van der Waals** loop for the equation of state,

$$P\left(\rho, T\right) = \frac{n k_B T}{1 - b' n} - a' n^2, \quad (17)$$

$$f = n k_B T \ln\left[\frac{\rho}{1 - b' n}\right] - a' n^2.$$

Fluctuating Hydrodynamics

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0 \tag{18}$$

$$\partial_t (\rho \mathbf{v}) + \nabla \cdot \left(\rho \mathbf{v}\mathbf{v}^{\mathrm{T}}\right) + \nabla \cdot \mathbf{\Pi} = \nabla \cdot (\boldsymbol{\sigma} + \mathbf{\Sigma}) \tag{19}$$

$$\partial_t (\rho E) + \nabla \cdot (\rho E \mathbf{v} + \mathbf{\Pi} \cdot \mathbf{v}) = \nabla \cdot (\psi + \mathbf{\Psi}) + \nabla \cdot ((\boldsymbol{\sigma} + \mathbf{\Sigma}) \cdot \mathbf{v}), \tag{20}$$

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

Momentum Fluxes

- The reversible contribution to the stress tensor is [5]

$$\mathbf{\Pi} = P\mathbf{I} - \left[\left(\kappa\rho\nabla^2\rho + \frac{1}{2}\kappa\left|\nabla\rho\right|^2\right)\mathbf{I}\right] - \left(\kappa\nabla\rho\otimes\nabla\rho\right) + \text{cross term?}$$

- Irreversible contribution to the stress is the viscous stress tensor

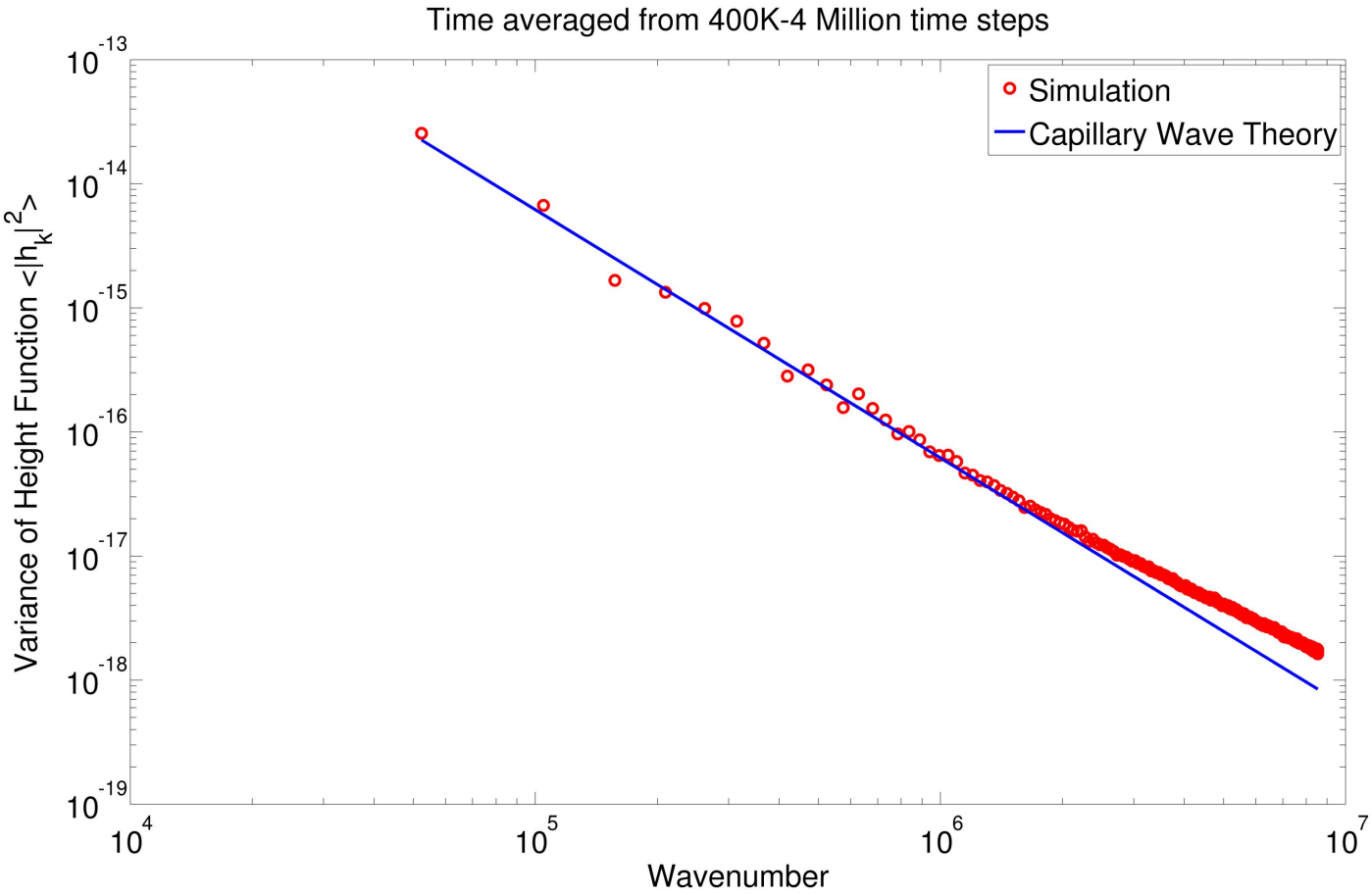
$$\boldsymbol{\sigma} = \eta\left(\nabla\mathbf{v} + (\nabla\mathbf{v})^{\mathrm{T}}\right) + \left(\zeta - \frac{2}{3}\eta\right)(\nabla\cdot\mathbf{v})\,\mathbf{I} \tag{21}$$

- Stochastic stress tensor obeys fluctuation-dissipation balance

$$\mathbf{\Sigma} = \sqrt{2\eta k_B T}\,\widetilde{\boldsymbol{\mathcal{W}}} + \left(\sqrt{\frac{\zeta k_B T}{3}} - \sqrt{\frac{2\eta k_B T}{3}}\right)\mathrm{Tr}\left(\widetilde{\boldsymbol{\mathcal{W}}}\right)\mathbf{I}, \tag{22}$$

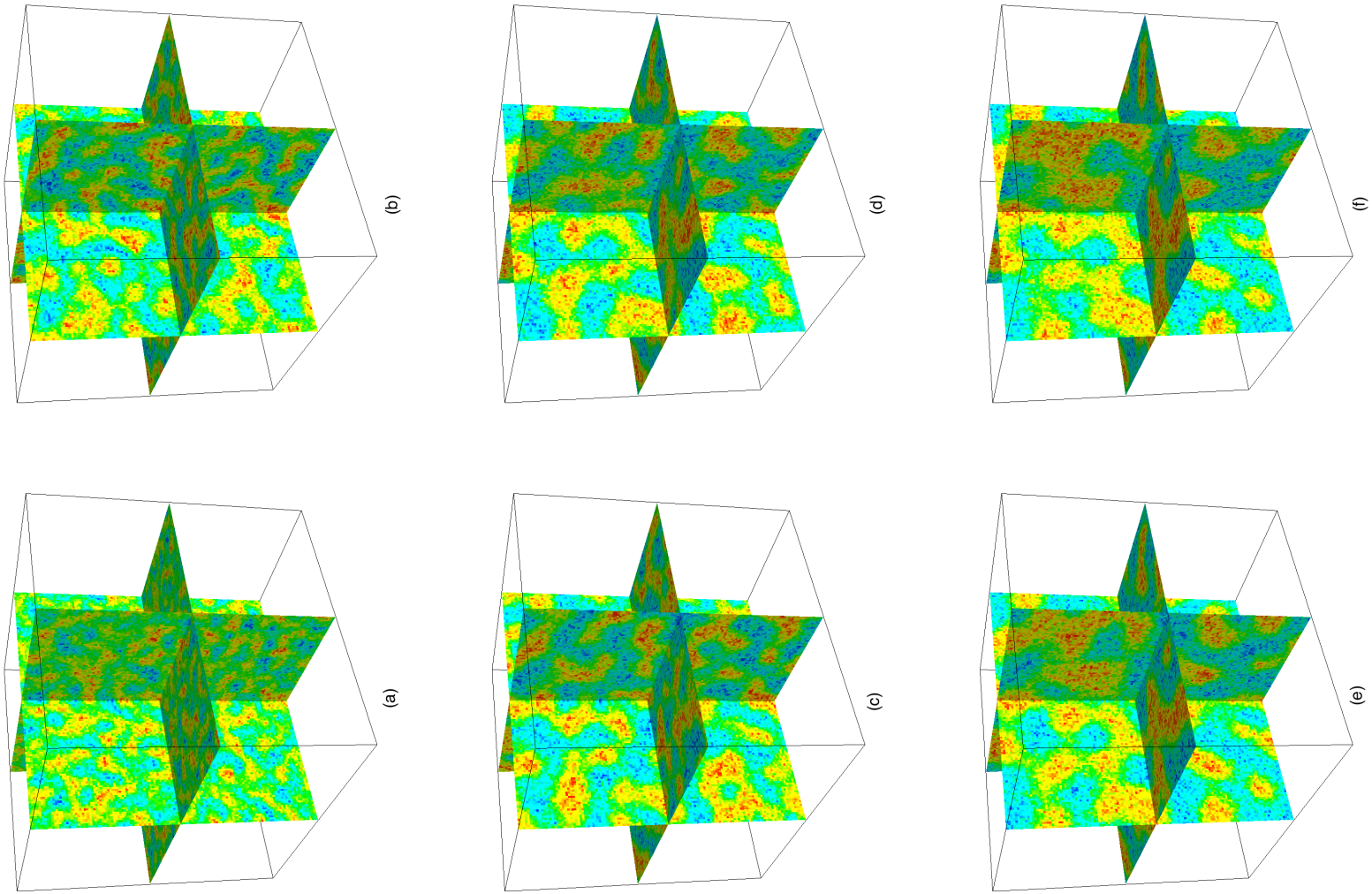
where $\widetilde{\boldsymbol{\mathcal{W}}} = (\boldsymbol{\mathcal{W}} + \boldsymbol{\mathcal{W}}^T)/\sqrt{2}$ is a symmetric white-noise tensor field.

Capillary Waves



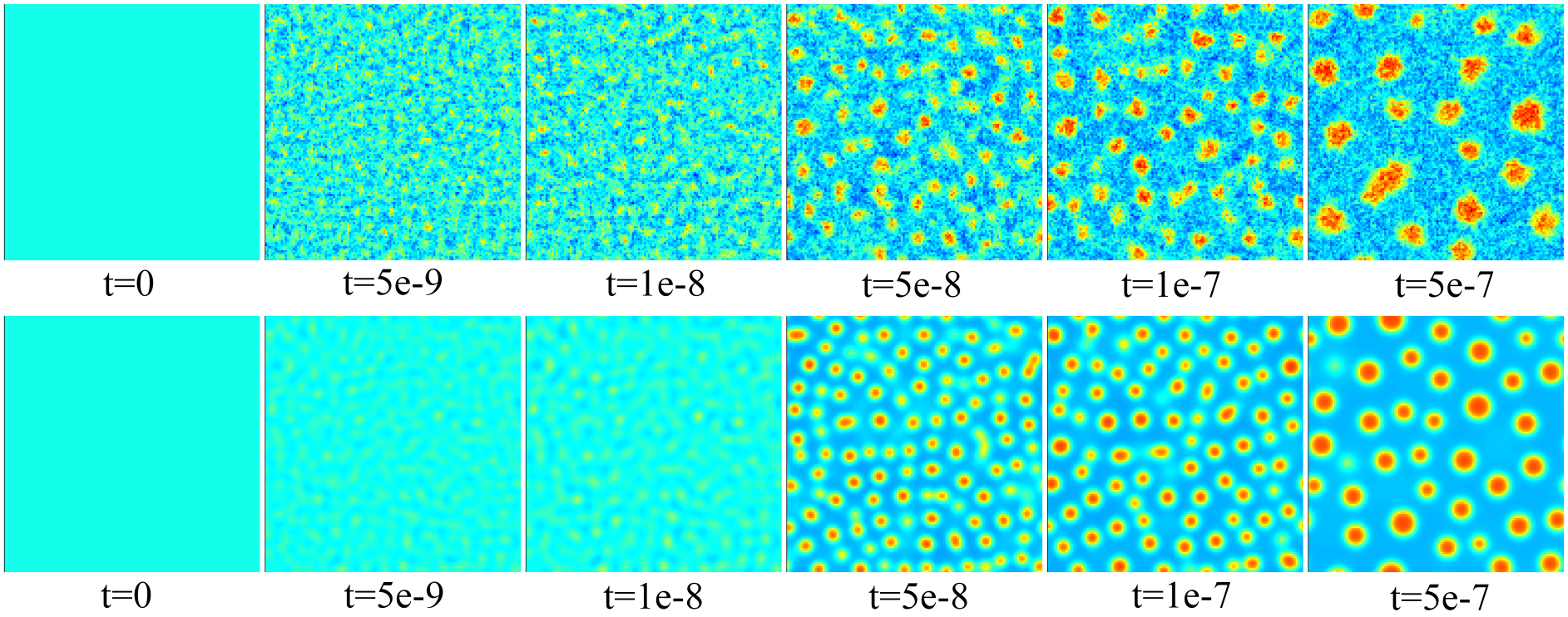
Variance of height fluctuations versus wavenumber comparing 2D simulations (red circles) and **capillary wave theory** (CWT) (black solid line).

Spinodal Decomposition



Spinodal decomposition in a near-critical Argon system at $\rho = 0.416$ g/cc, $T = 145.85$ K leading to a **bicontinuous pattern**.

Condensation



Liquid-vapor spinodal decomposition in a near-critical van der Waals Argon system at $\rho = 0.36\ \mathrm{g/cc}$, $T = 145.85\ \mathrm{K}$ leading to **droplets** forming in a majority vapor phase.

Chemically-Reactive Mixtures

- The species density equations for a mixture of N_{S} species are given by

$$\frac{\partial}{\partial t}\left(\rho_s\right) + \nabla \cdot \left(\rho_s \mathbf{v} + \mathbf{F}\right) = m_s \Omega_s, \qquad (s = 1, \ldots N_{\mathrm{S}}) \tag{23}$$

- Due to mass conservation $\rho = \sum_s \rho_s$ follows the continuity equation,

$$\frac{\partial}{\partial t}\rho + \nabla \cdot (\rho \mathbf{v}) = 0. \tag{24}$$

- The mass fluxes take the form, excluding barodiffusion and thermodiffusion,

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

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

Multispecies Mass Diffusion

- $\mathbf{\Gamma}$ is a matrix of thermodynamic factors,

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

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

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

- We, however, do not know values of these for even a single ternary mixture!

  We have studied **ideal mixtures**: hard-sphere **gas mixtures [6]** and **dilute solutions** of salt+sugar in water [7].

Chemistry

- Consider a system with $N_{\rm R}$ **elementary reactions** with reaction r

$$\mathfrak{R}_r: \qquad \sum_{s=1}^{N_{\rm S}} \nu_{sr}^{+} \mathfrak{M}_s \rightleftarrows \sum_{s=1}^{N_{\rm S}} \nu_{sr}^{-} \mathfrak{M}_s$$

  The **stoichiometric coefficients** are $\nu_{sr} = \nu_{sr}^{-} - \nu_{sr}^{+}$ and mass conservation requires that $\sum_s \nu_{sr} m_r = 0$.
- 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**

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

Chemistry

- The mass production due to chemistry can take **one of two forms** [8]:

$$\Omega_s = \sum_r \nu_{sr} \left(\frac{P}{\tau_r k_B T} \right) \hat{\mathcal{A}}_r \text{ (deterministic LMA)} \qquad (25)$$

$$+ \sum_r \nu_{sr} \begin{cases} \left(2 \frac{P}{\tau_r k_B T} \frac{\hat{\mathcal{A}}_r}{\mathcal{A}_r} \right)^{\frac{1}{2}} \diamond \boldsymbol{\mathcal{Z}}(\mathbf{r}, t) & \text{log-mean eq. (LME)} \\ \left(\frac{P}{\tau_r k_B T} \prod_s e^{\nu_{sr}^+ \hat{\mu}_s} \right)^{\frac{1}{2}} \boldsymbol{\mathcal{Z}}(\mathbf{r}, t) & \text{chemical Langevin eq. (CLE)} \end{cases}$$

- The **LME** follows the correct structure of Langevin equations (GENERIC structure of Ottinger/Grmela). Is **time-reversible** (obeys detailed balance) **at thermodynamic equilibrium** wrt to the Einstein distribution.
- The **CLE** follows from a truncation of the Kramers-Moyal expansion at second order. No true thermodynamic equilibrium since it assumes **one-way reactions**.
- **Which one is correct? Neither!**

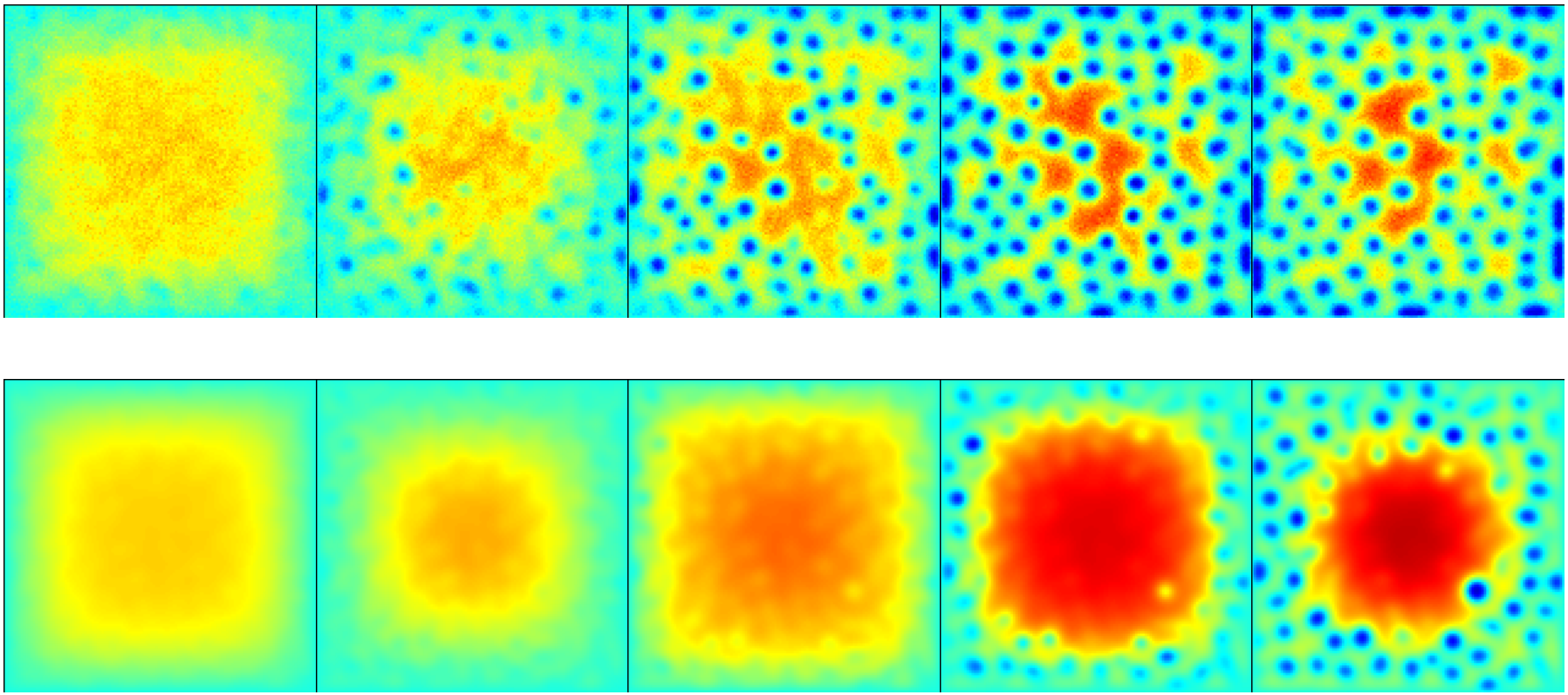
Nonlinear Chemical Networks

We have studied the Baras-Pearson-Mansour (BPM) model $\mathfrak{M} = (U, V, W, S, U_f, V_f)$,

$$\begin{aligned} \mathfrak{R}_1 : &\quad U + W \leftrightarrows V + W \\ \mathfrak{R}_2 : &\quad V + V \leftrightarrows W + S \\ \mathfrak{R}_3 : &\quad V \leftrightarrows S \\ \mathfrak{R}_4 : &\quad U \leftrightarrows U_f \\ \mathfrak{R}_5 : &\quad V \leftrightarrows V_f \end{aligned} \tag{26}$$

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).

Poisson Noise

- The reason neither LME nor CLE are correct is that **there is no S(P)DE** that can correctly describe both the short-time (typical) and long-time (rare event) behavior of the master equation.
- This is related to the fact that the central limit theorem and large-deviation theory are not consistent with the same nonlinear S(P)DE.
- One must either use the **Chemical Master Equation (CME)** with SSA/Gillespie (microscopic rather than macroscopic), **or**
- One can use **Poisson noise** instead of **Gaussian noise** using **tau leaping**.
  This can be thought of as a **coarse-graining in time** of the original jump process described by the CME.
- Quite generally the appropriateness of assuming Gaussian white noise for the stochastic fluxes is questionable.

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