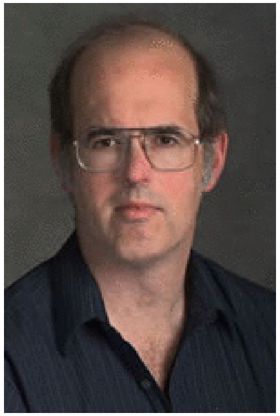
Modeling of Thermal Fluctuations in Multicomponent Reacting Systems

Kaushik Balakrishnan
Lawrence Berkeley Lab

John B. Bell
Lawrence Berkeley Lab

Aleksandar Donev
New York University

Alejandro L. Garcia
San Jose State University



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Fluctuating Navier-Stokes

Thermal fluctuations in a fluid may be modeled by adding white-noise terms in the dissipative fluxes, as in the stress tensor for the Navier-Stokes equation.

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla \cdot \left[\rho \mathbf{v}\mathbf{v}^T + p\mathbf{I}\right] + \nabla \cdot \mathbf{\Pi} = \rho \mathbf{g}$$

Navier-Stokes

$$\overline{\mathbf{\Pi}}_{\alpha\beta} = -\eta \left(\frac{\partial v_\alpha}{\partial x_\beta} + \frac{\partial v_\beta}{\partial x_\alpha} \right) - \delta_{\alpha\beta} \left(\kappa - \frac{2}{3}\eta \right) \nabla \cdot \mathbf{v}$$

Deterministic Stress Tensor

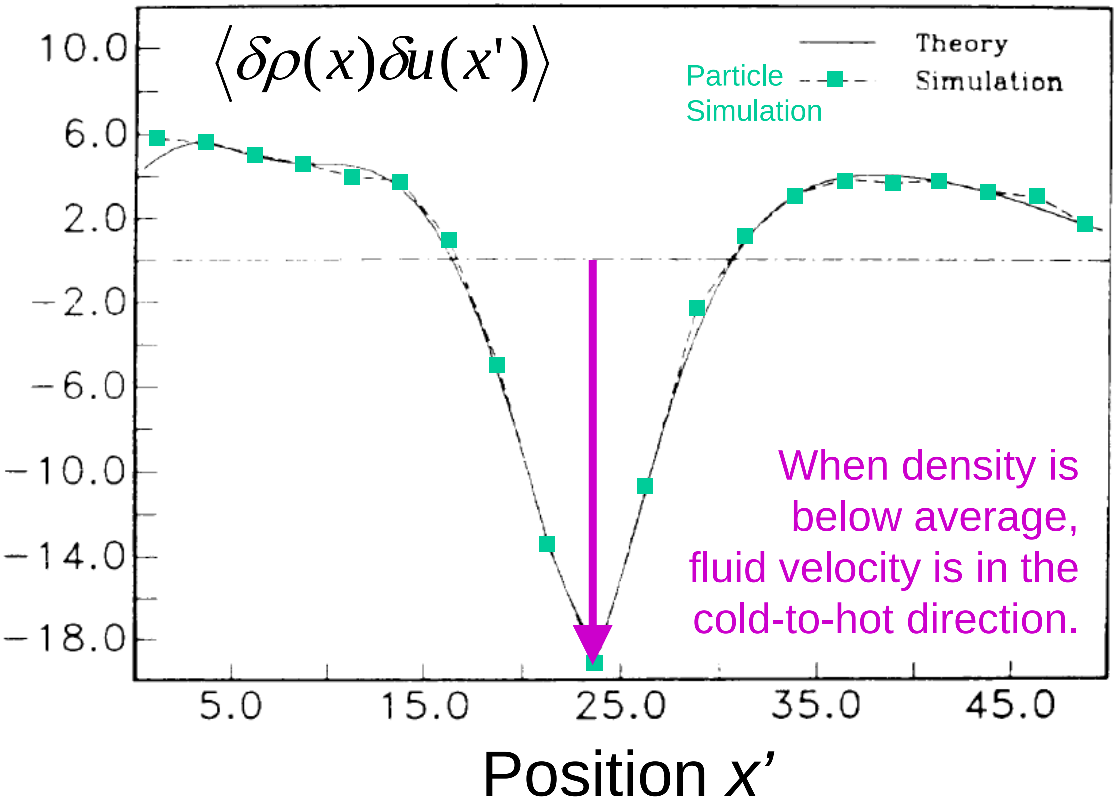
Covariance of Stochastic Stress Tensor

$$\langle \widetilde{\mathbf{\Pi}}_{\alpha\beta}(\mathbf{r},t) \widetilde{\mathbf{\Pi}}_{\gamma\delta}(\mathbf{r}',t') \rangle =$$

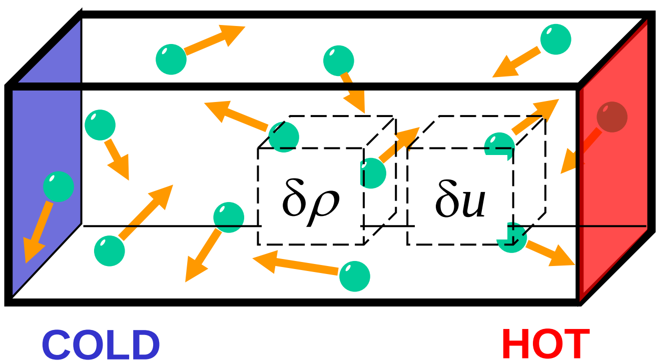
$$2k_B T \left[\eta(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) + (\kappa - \tfrac{2}{3}\eta)\delta_{\alpha\beta}\delta_{\gamma\delta} \right] \delta(t-t')\delta(\mathbf{r}-\mathbf{r}')$$

Density-Velocity Correlation

Correlation of density-velocity fluctuations under ∇T



Line is numerical solution Landau-Lifshitz fluctuating hydrodynamics



ALG, *Phys. Rev. A* **34** 1454 (1986).
ALG, M. Malek Mansour, G. Lie and E. Clementi,, *J. Stat. Phys.* **47** 209 (1987).

Fluctuating Hydrodynamic Solvers

Have simple, accurate, and efficient finite volume schemes for the stochastic PDEs of fluctuating hydrodynamics.

$$
\begin{aligned}
U_j^{n+\frac{1}{3}} &= U_j^n + \Delta U_j(U^n, W_1) \quad (\text{estimate at } t = (n+1)\Delta t\ ) \\
U_j^{n+\frac{2}{3}} &= \frac{3}{4}U_j^n + \frac{1}{4}\left[U_j^{n+\frac{1}{3}} + \Delta U_j(U_j^{n+\frac{1}{3}}, W_2)\right] \quad (\text{estimate at } t = (n+\frac{1}{2})\Delta t\ ) \\
U_j^{n+1} &= \frac{1}{3}U_j^n + \frac{2}{3}\left[U_j^{n+\frac{2}{3}} + \Delta U_j(U^{n+\frac{2}{3}}, W_3)\right],
\end{aligned}
$$

3rd Order Runge-Kutta

where

$$
\underbrace{\Delta U_j(U, W)}_{\text{Change in Mass, Momentum, Energy}} = -\frac{\Delta t}{\Delta x}\left[\underbrace{F_{j+\frac{1}{2}}(U) - F_{j-\frac{1}{2}}(U)}_{\text{Deterministic Flux}}\right] + \frac{\Delta t^{1/2}}{\Delta x^{3/2}}\underbrace{\left(Z_{j+\frac{1}{2}} - Z_{j-\frac{1}{2}}\right)}_{\text{Stochastic Flux}}.
$$

J.B. Bell, ALG, and S. Williams, *Physical Review E* 76 016708 (2007)
A. Donev, E. Vanden-Eijnden, ALG, and J. B. Bell, *CAMCoS*, 5(2):149-197, (2010)

Multi-Species Fluid Equations

Hydrodynamic equation for the mass densities, ρ_k, in a multi-species fluid have the form,

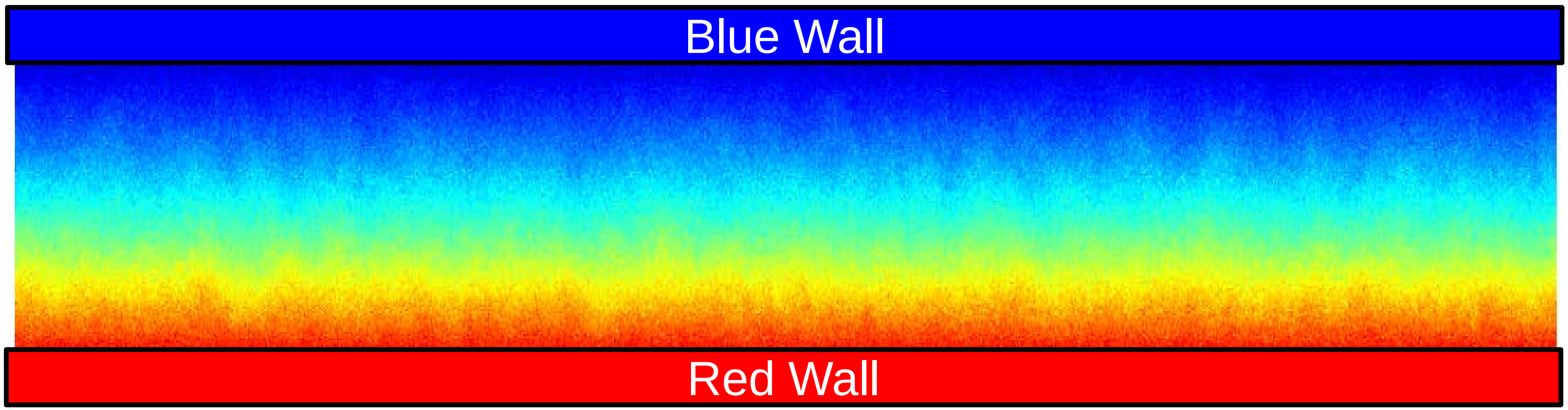
$$\frac{\partial}{\partial t}(\rho_k) + \nabla \cdot (\rho_k \mathbf{v}) + \nabla \cdot \boldsymbol{\mathcal{F}}_k = 0$$

Mass conservation requires that,

$$\sum_{k=1}^{N_s} \boldsymbol{\mathcal{F}}_k = 0 \quad \xRightarrow{\text{so}} \quad \frac{\partial}{\partial t}\rho + \nabla \cdot (\rho \mathbf{v}) = 0$$

Binary Diffusion & Fluctuations

Consider a monatomic gas of “red” and “blue” particles with a steady state gradient imposed by wall boundaries.

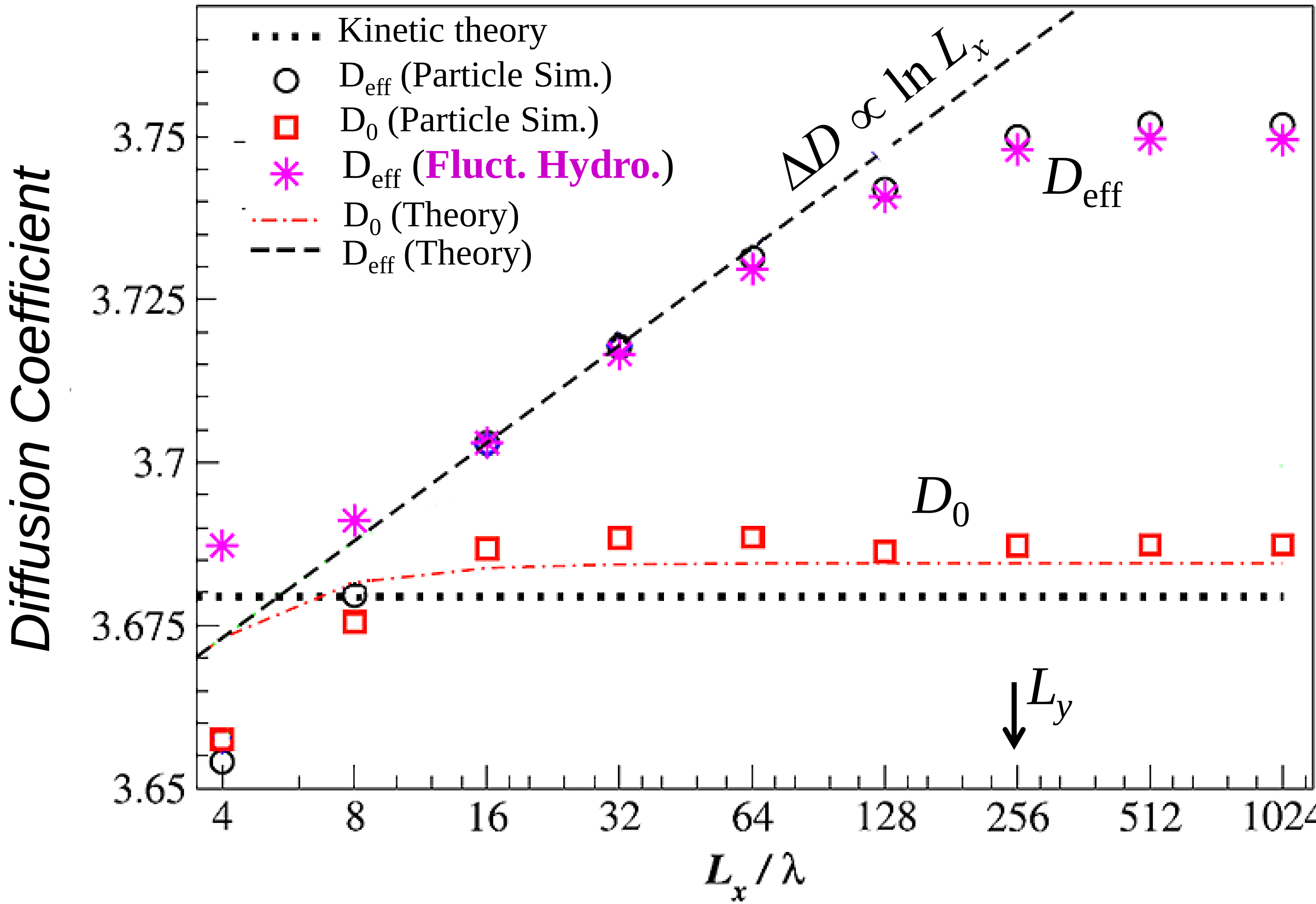


The non-equilibrium correlation $\langle \delta\hat{c}\,\delta\hat{u}_{\parallel} \rangle$ enhances the effective flux of concentration even at this steady state.

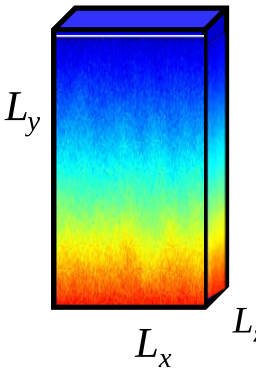
A. Donev, ALG, A. de la Fuente, and J.B. Bell, *J. Stat. Mech.* 2011:P06014 (2011)

A. Donev, ALG, A. de la Fuente, and J.B. Bell, *Phys. Rev. Lett.*, 106(20): 204501 (2011)

Binary Diffusion Enhancement



Quasi-2D ($L_z << L_y$)



$L_y = 256\ \lambda$
$L_z = 2\ \lambda$

Species Flux (Deterministic)

Deterministic species flux has two contributions,

$$\overline{\boldsymbol{\mathcal{F}}}_k = \underbrace{-\rho Y_k \theta_k \frac{\nabla T}{T}}_{\text{Thermal Diffusion}} \underbrace{- \sum_{l=1}^{N_s} C_{kl} \mathbf{d}_l}_{\text{Multicomponent Diffusion}}$$

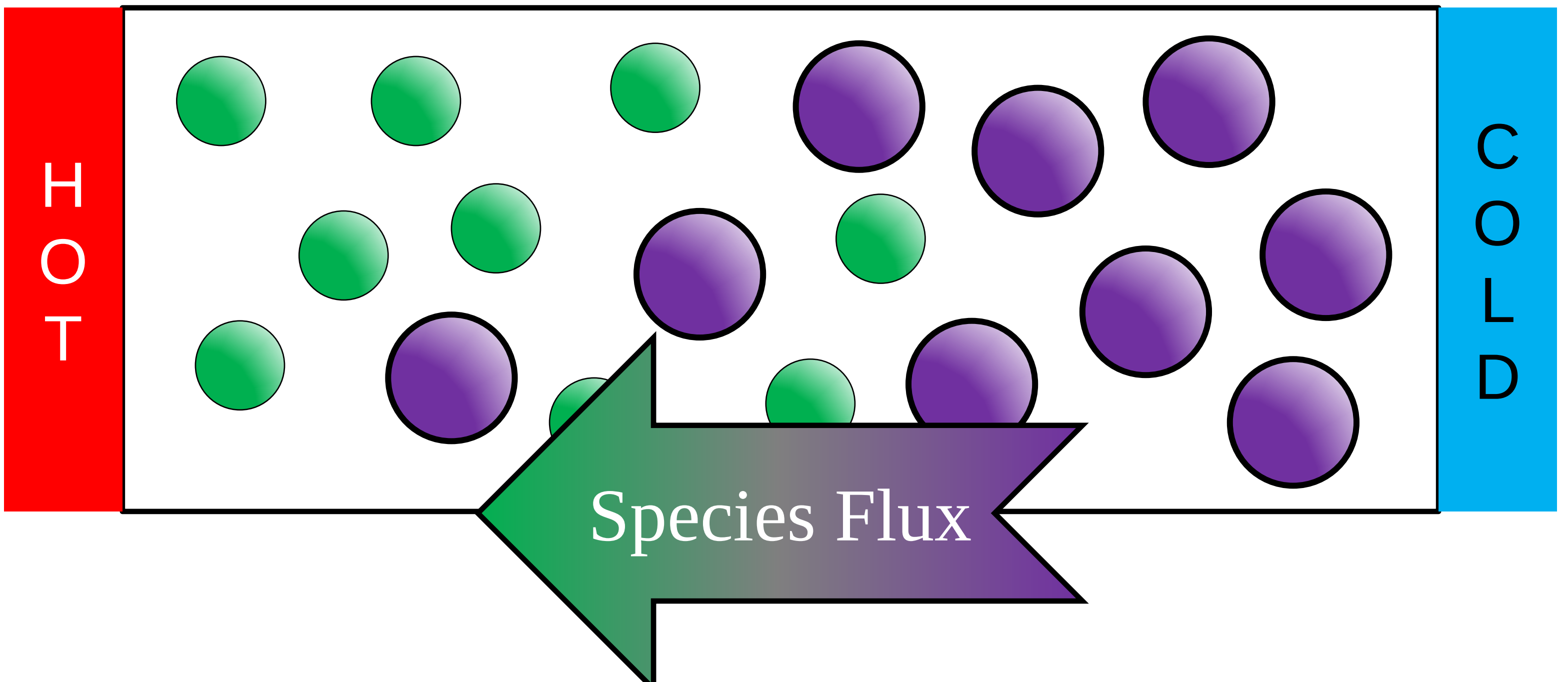
where the species diffusion driving force is,

$$\mathbf{d}_k = \nabla X_k + (X_k - Y_k) \frac{\nabla p}{p}$$

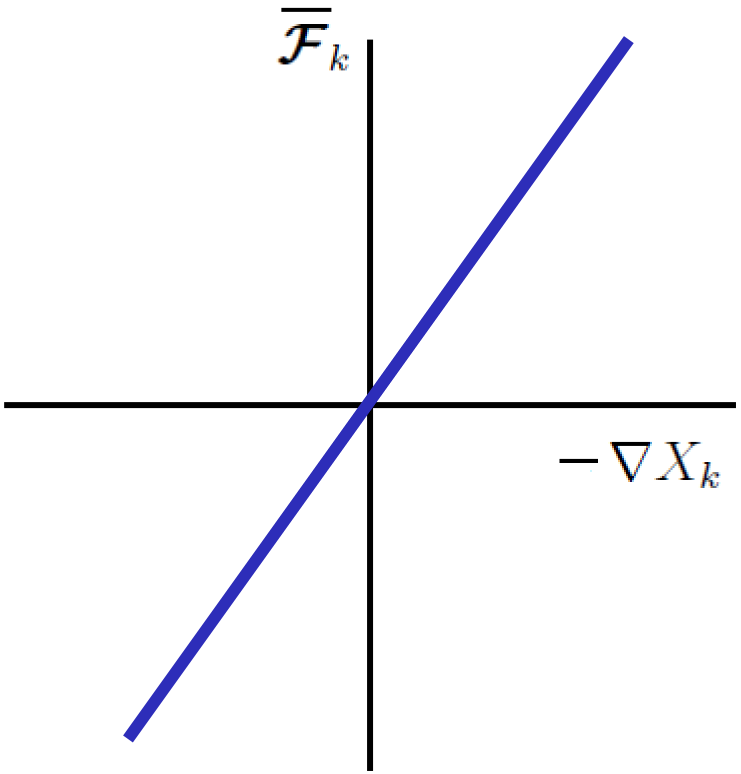
Note that for constant pressure, $\mathbf{d}_k = \nabla X_k$

Soret Effect

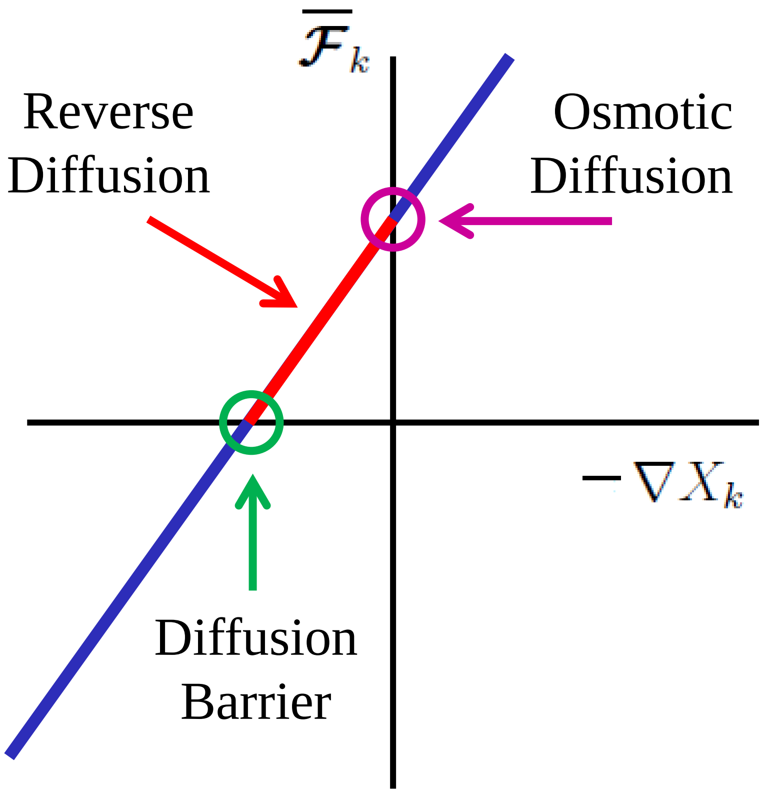
Thermal diffusion produces the Soret effect in which a temperature gradient induces a concentration flux.



Diffusion Interaction Effects



Binary Diffusion:
One Coefficient



Ternary Diffusion:
Three Coefficients

Energy Equation

The hydrodynamic equation for energy density is,

$$\frac{\partial}{\partial t}(\rho E) + \nabla \cdot [(\rho E + p)\mathbf{v}] + \nabla \cdot [\boldsymbol{\mathcal{Q}} + \mathbf{\Pi} \cdot \mathbf{v}] = \rho \mathbf{v} \cdot \mathbf{g}$$

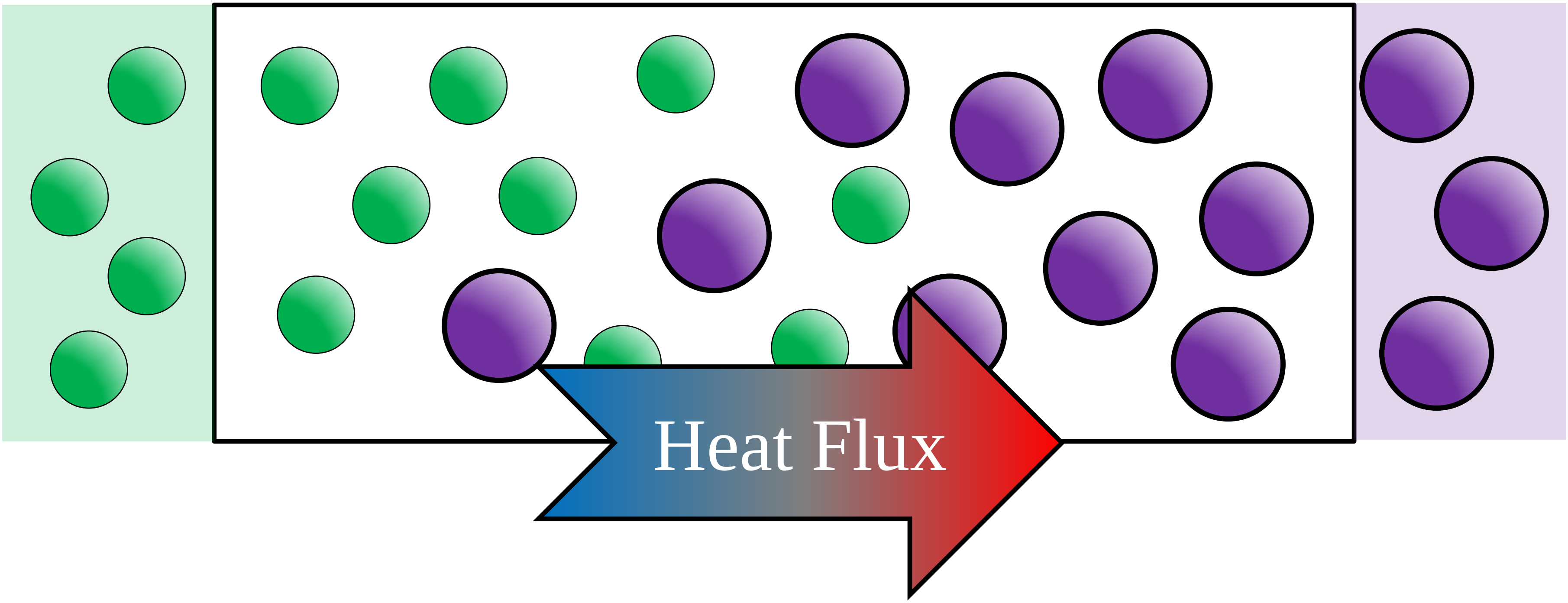
Heat Flux

The deterministic heat flux has three terms, two of which are linked to the species flux,

$$\overline{\boldsymbol{\mathcal{Q}}} = \underbrace{-\lambda^* \nabla T}_{\text{Thermal Conductivity}} \underbrace{- p \sum_{k=1}^{N_s} \theta_k \mathbf{d}_\mathbf{k}}_{\text{Thermal Diffusion}} + \underbrace{\sum_{k=1}^{N_s} h_k \overline{\boldsymbol{\mathcal{F}}}_k}_{\text{Enthalpy Diffusion}}$$

Dufour Effect

By Onsager reciprocity, thermal diffusion also gives the Dufour effect in which a concentration gradient induces an energy flux.



Irreversible Thermodynamics

Due to the coupling of the species density and energy fluxes their stochastic fluxes are correlated. To formulate these we write the entropy production rate,

$$\mathfrak{v} = -\frac{1}{T^2}\boldsymbol{\mathcal{Q}}' \cdot \nabla T - \frac{1}{T}\sum_{i=1}^{N_s} \boldsymbol{\mathcal{F}}_i \cdot \nabla_T \mu_i$$

where

$$\nabla_T \;\; \mu_i(p,T,Y_i) = \nabla \mu_i - \left(\frac{\partial \mu_i}{\partial T}\right)_{p,Y_i} \nabla T$$

$$\boldsymbol{\mathcal{Q}}' = \boldsymbol{\mathcal{Q}} - \sum_{k=1}^{N_s} h_k \boldsymbol{\mathcal{F}}_k$$

Note: By Curie principle the stress tensor is not coupled to these fluxes

Phenomenological Laws

We now formulate this as,

$$\mathfrak{v} = \mathbf{J}^T \mathbf{X} = \mathbf{X}^T \boldsymbol{\mathfrak{L}}^T \mathbf{X}.$$

with the fluxes and thermodynamic forces,

$$\mathbf{J} = \begin{bmatrix} \mathcal{F} \\ \mathcal{Q}' \end{bmatrix} \quad \text{and} \quad \mathbf{X} = \begin{bmatrix} -\frac{1}{T}\nabla_T(\mu_i - \mu_{N_s}) \\ -\frac{1}{T^2}\nabla T \end{bmatrix}$$

Species Diffusion

related via the phenomenological laws,

$$\mathbf{J} = \boldsymbol{\mathfrak{L}}\mathbf{X}$$

$$\boldsymbol{\mathfrak{L}} = \begin{bmatrix} \mathbf{L} & \mathbf{l} \\ \mathbf{l}^T & \ell \end{bmatrix}$$

Thermal Diffusion

Thermal Conduction

Fluctuation-Dissipation

The stochastic fluxes are written as,

$$\widetilde{\mathbf{J}}_\alpha = \begin{bmatrix} \widetilde{\boldsymbol{\mathcal{F}}}_\alpha \\ \widetilde{\boldsymbol{\mathcal{Q}}}'_\alpha \end{bmatrix} \quad \text{and} \quad \tilde{\mathbf{J}}_\alpha = \mathcal{B}\mathbf{W}^{(\alpha)} \quad \text{where} \quad \mathcal{B} = \begin{bmatrix} \mathbf{B} & 0 \\ \mathbf{b}^T & \beta \end{bmatrix}$$

White noise

from fluctuation-dissipation we have,

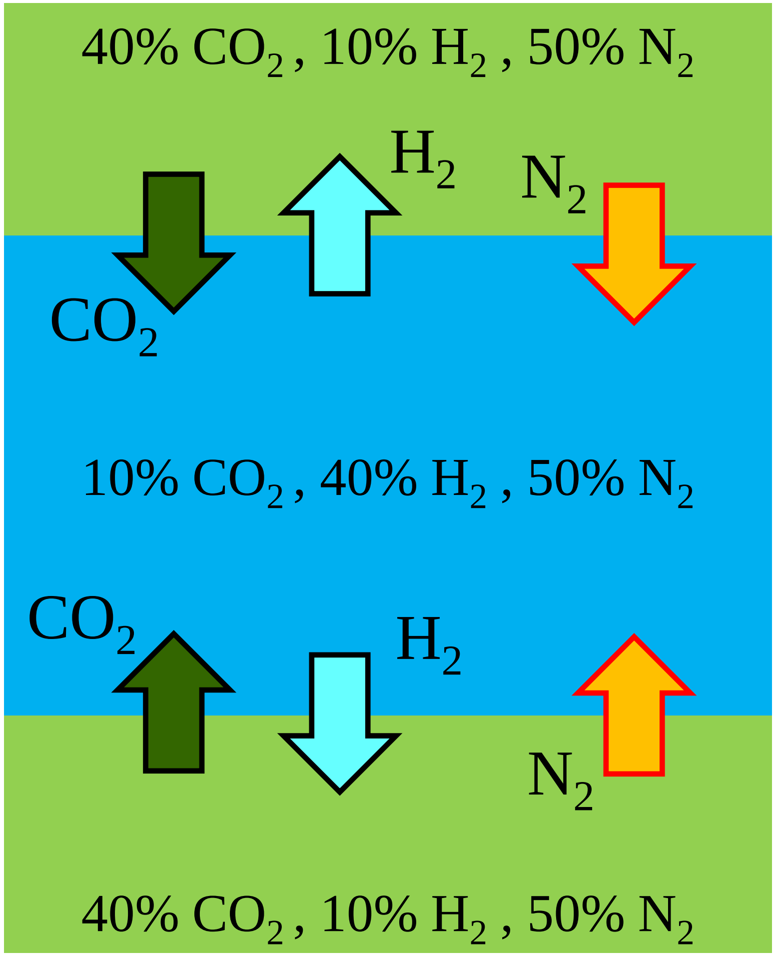
$$\langle \widetilde{\mathbf{J}}_\alpha(\mathbf{r},t)\widetilde{\mathbf{J}}_\beta^T(\mathbf{r}',t')\rangle = 2k_B\,\mathfrak{L}\,\delta_{\alpha\beta}\,\delta(x_\alpha - x'_\beta)\delta(t-t')$$

so we can find $\mathcal{B}$ by solving,

$$2k_B\mathfrak{L} = \mathcal{B}\mathcal{B}^T$$

Reverse Diffusion Example

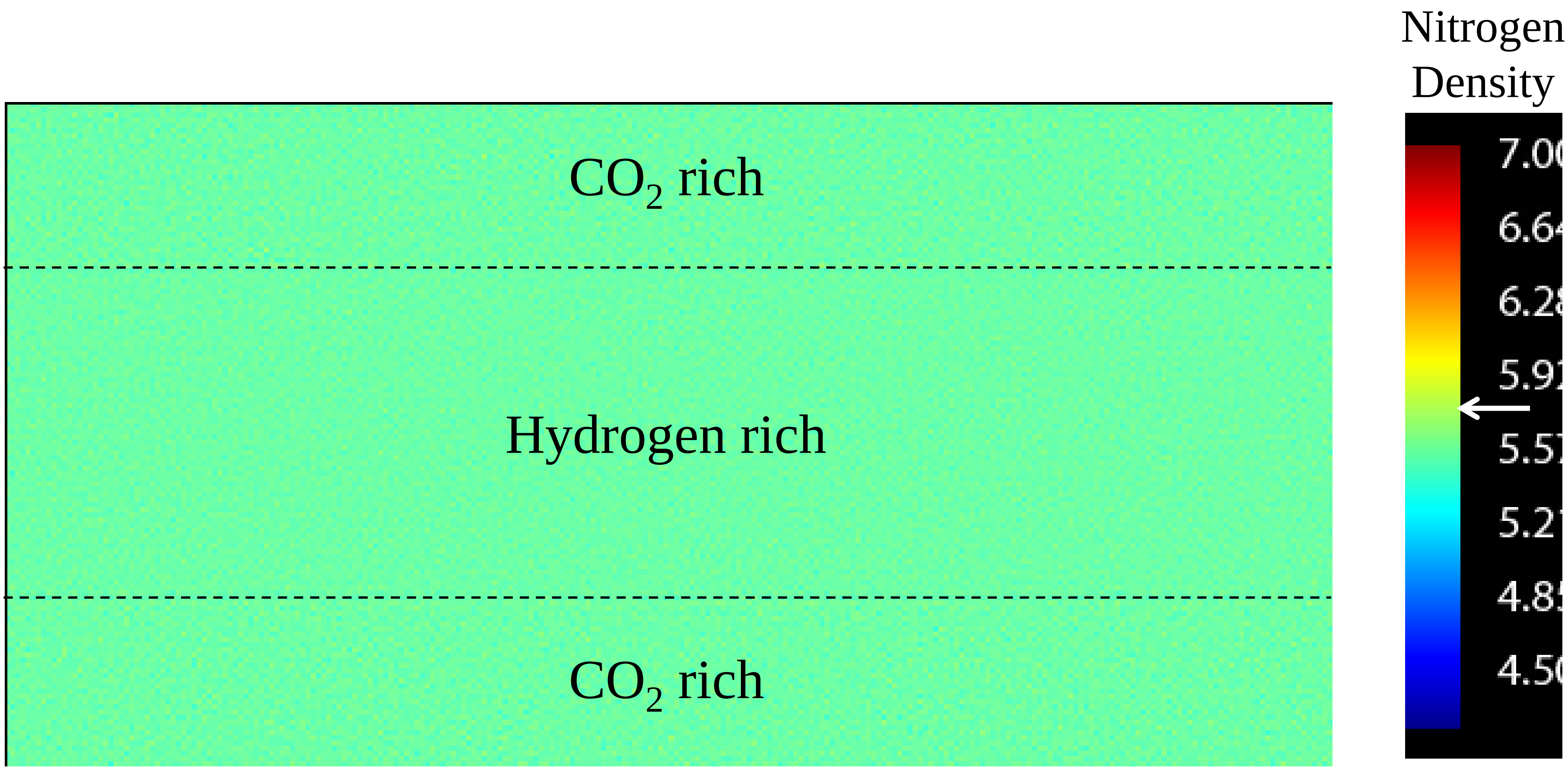
In this set-up the hydrogen and carbon dioxide have normal diffusion while nitrogen exhibits reverse diffusion, resulting in a pumping of nitrogen to the center of the system.



Duncan and Toor, *AIChE J.*, **8** 38-41 (1962)

No gravity

Reverse Diffusion Example



Initial nitrogen density = 5.7

Fluctuating Chemistry

For chemical reaction of the general form,

$$\sum_{k=1}^{N_s} r_{k,l} \mathsf{S}_k \xrightarrow{K_l} \sum_{k=1}^{N_s} p_{k,l} \mathsf{S}_k \qquad\qquad l = 1, \ldots, M_r$$

The deterministic source term in the species equation for ρ_k is

$$\Omega_k = \sum_{l=1}^{M_r} \nu_{k,l} W_k K_l \prod_{i=1}^{N_s} \left(\frac{\rho_k}{W_k} \right)^{r_{i,l}} \qquad\qquad \nu_{k,l} = p_{k,l} - r_{k,l}$$

and the stochastic (Langevin) source term is

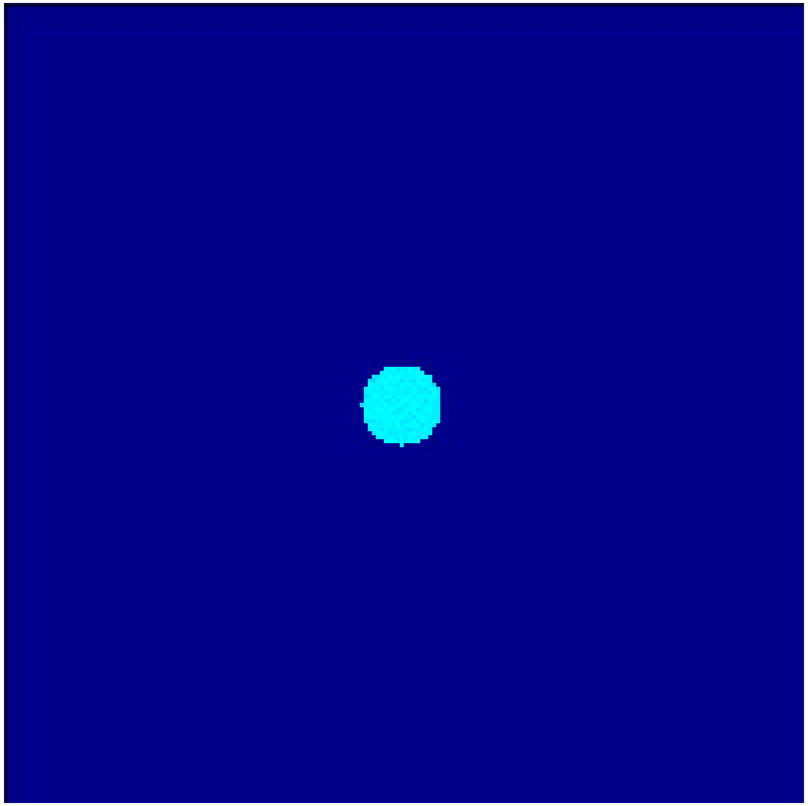
$$\tilde{\Omega}_k = \sum_{l=1}^{M_r} \nu_{k,l} W_k \sqrt{ \frac{K_l}{N_A} \prod_{i=1}^{N_s} \left(\frac{\rho_k}{W_k} \right)^{r_{i,l}} } \, \mathrm{W}_l$$

White noise

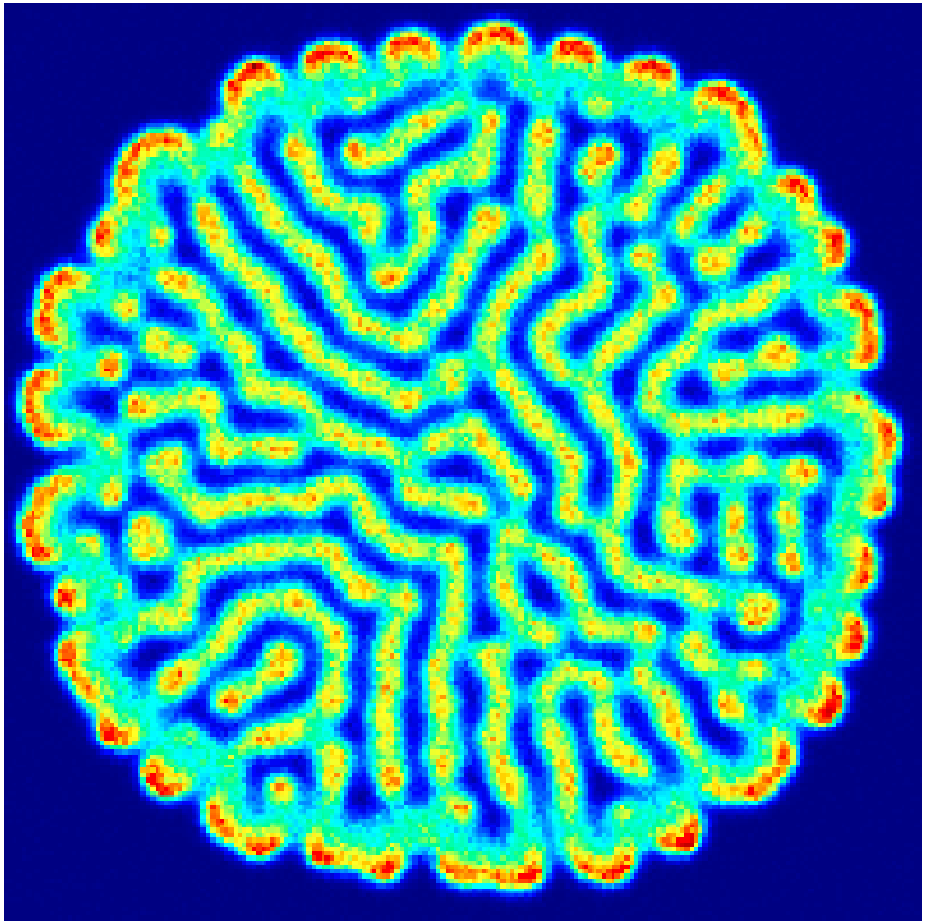
Turing Pattern Instability

Use the Schlogl chemistry model, initializing the center region at the ‘+’ state and the rest of the system in the ‘0’ state.

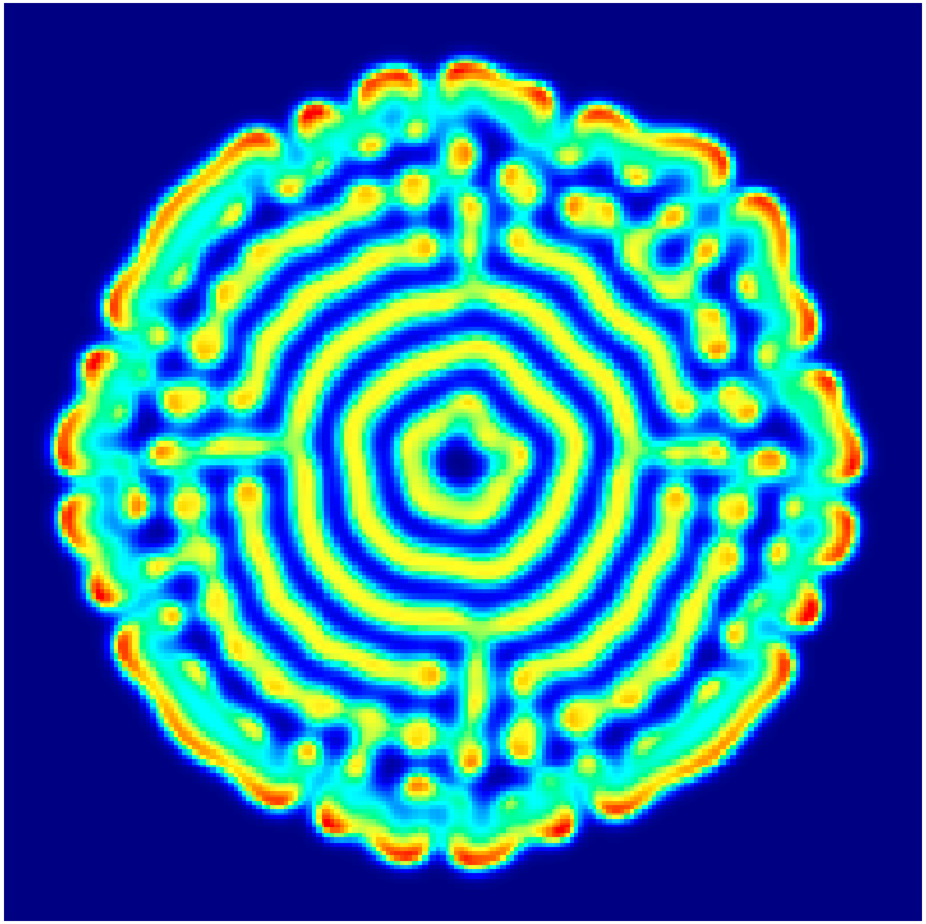
This produces an evolving chemical wave front and in the wake of the front a Turing instability produces labyrinth patterns.



Turing Pattern Instability



With Fluctuations

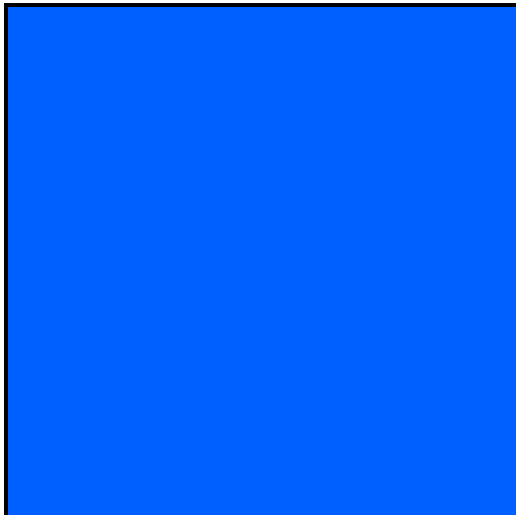


Without Fluctuations

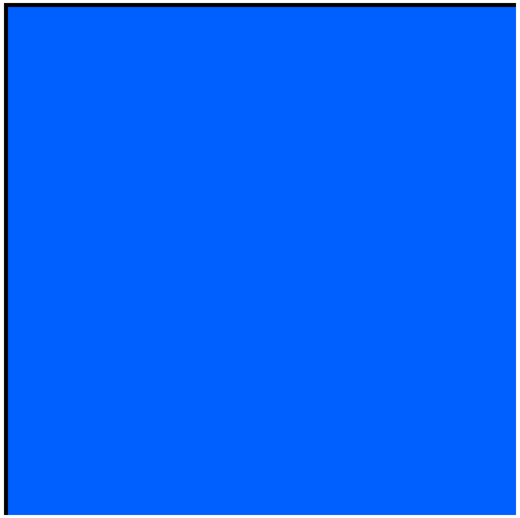
Liquid-Vapor Modeling

Extending simulations to include multi-phase fluids by using the van der Waals equation of state with corresponding surface tension contribution in the momentum equation.

With Fluctuations



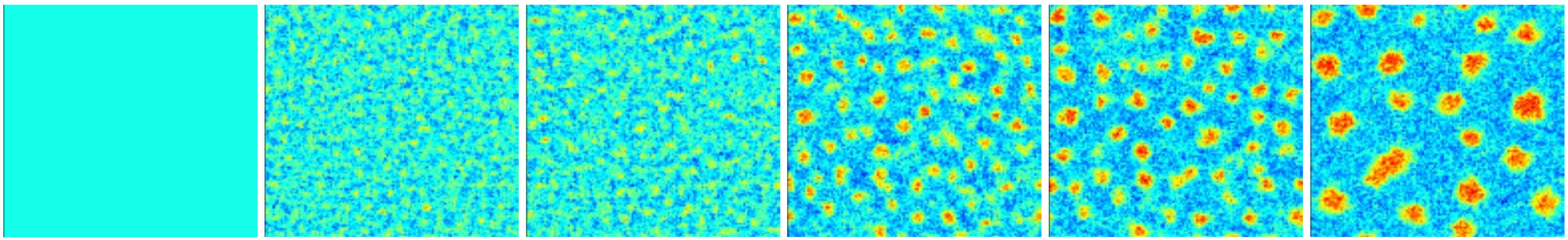
Without Fluctuations



With Anuj Chaudhri

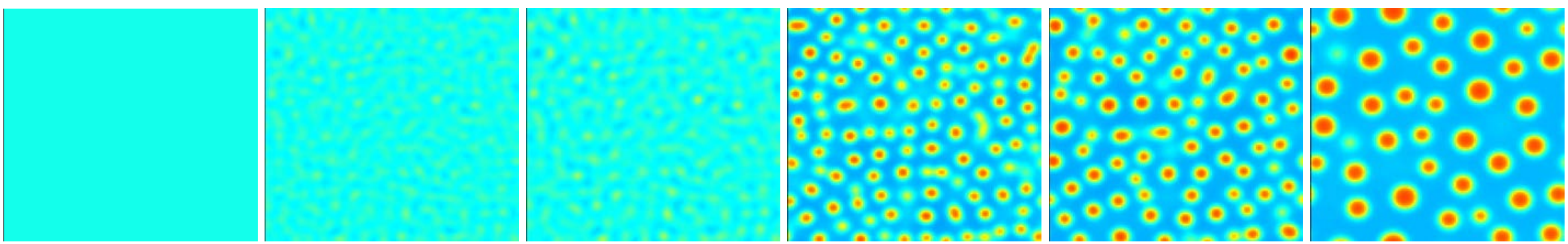
Spinodal Decomposition

With Fluctuations



t=0 t=50000 t=100000 t=500000 t=1000000 t=5000000

Without Fluctuations



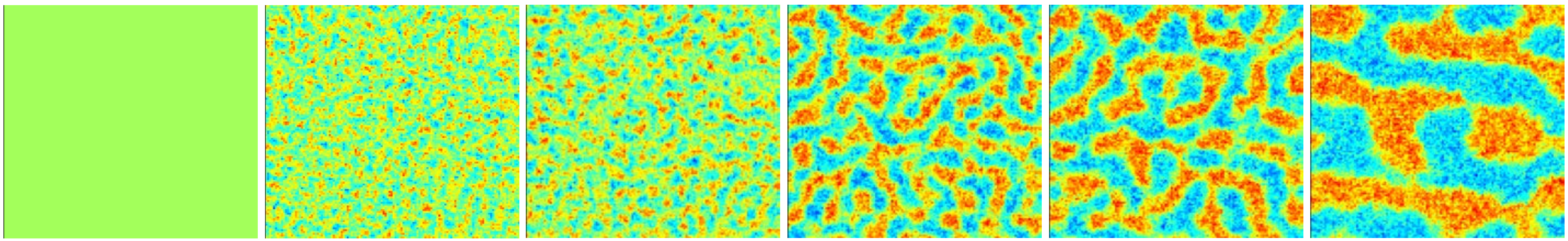
t=0 t=50000 t=100000 t=500000 t=1000000 t=5000000

Droplets in off-critical quench with initial $\rho = 0.87\ \rho_{critical}$

t = number of time steps

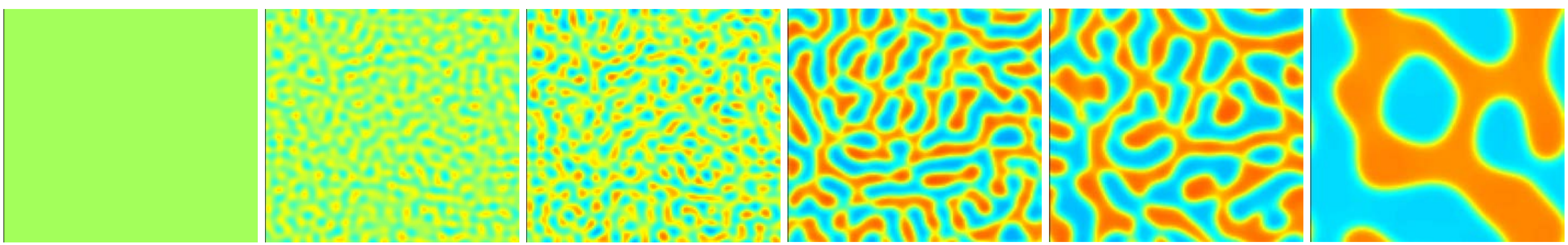
Spinodal Decomposition

With Fluctuations



t=0 t=50000 t=100000 t=500000 t=1000000 t=5000000

Without Fluctuations



t=0 t=50000 t=100000 t=500000 t=1000000 t=5000000

Bicontinuous patterns in critical quench with initial $\rho = \rho_{critical}$

t = number of time steps

Future Work

- Developing incompressible and low-Mach number schemes for fluctuating hydrodynamics

- Extensions to more complex fluids

- Exploring particle/SPDE hybrids using Adaptive Mesh and Algorithm Refinement

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