Modeling fluctuations in multicomponent systems

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Materials for a Sustainable Energy Future
Workshop II: Fuels form Sunlight Los Angeles, CA
October 14-18, 2013

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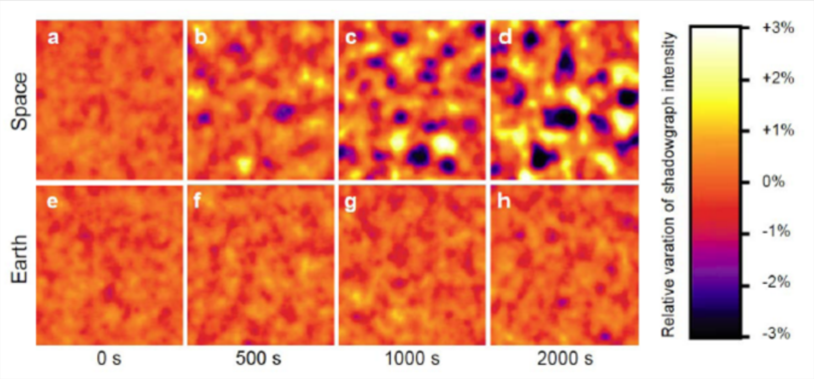
Mesoscale models of fluid flow

Most computations of fluid flows use a continuum representation (density, pressure, etc.) for the fluid.

- Dynamics described by set of PDEs – Navier Stokes equations
  - Mass
  - Momentum
  - Energy
  - Any additional phenomena
- Well-established numerical methods (finite difference, finite elements, etc.) for solving these PDEs.
- Hydrodynamic PDEs are accurate over a broad range of length and time scales.

But at some scales the continuum representation breaks down a different description is needed

Giant fluctuations



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Experiments show significant concentration fluctuations in zero gravity

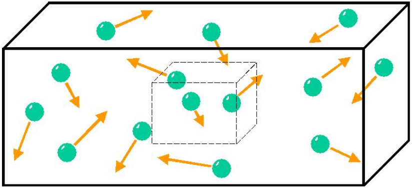
Fluctuations are reduced by gravity; cut-off wavelength proportional to $g^{-1/4}$

Vailati, *et al.*, Nature Comm., 2:290 (2011)

Thermal Fluctuations

The structures seen in experiments arise because of thermal fluctuations

- At microscopic scales, fluids are particle systems
  - Hydrodynamic variables, mass, momentum, energy, etc., correspond to averages of particle representation over representative volumes
  - Hydrodynamic variables naturally fluctuate
- In non-equilibrium settings, fluctuations lead to long-range correlations in hydrodynamic variables



Particle schemes (DSMC, MD, ...) capture statistical structure of fluctuations in macroscopic variables

- Variance of fluctuations
- Time-correlations
- Non-equilibrium behavior

But that are too expensive to use to study problems at these scales

Modeling fluctuations at the continuum level

Can / should we capture fluctuations at the continuum level?

- Important part of dynamics at mesoscale
- Essential ingredient of hybrid multiscale algorithms (coupled continuum and atomistic)

- Landau and Lifshitz proposed model for fluctuations at the continuum level
  - Incorporate stochastic fluxes into compressible Navier Stokes equations
  - Magnitudes set by fluctuation dissipation balance
- Generalized formulation for binary mixtures by Cohen and Law and Nieuwoudt.

Want to extend fluctuating Navier Stokes to general multicomponent systems.

Landau-Lifshitz fluctuating Navier Stokes

- Incorporate stochastic fluxes into compressible Navier Stokes equations
- Equilibrium fluctuations known from statistical mechanics
- Magnitudes set by fluctuation dissipation balance

$$\partial \mathbf{U}/\partial t + \nabla\cdot\mathbf{F} = \nabla\cdot\mathbf{D} + \nabla\cdot\mathbf{S} \quad \text{where} \quad \mathbf{U} = \begin{pmatrix} \rho \\ \rho\mathbf{v} \\ \rho E \end{pmatrix}$$

$$\mathbf{F} = \begin{pmatrix} \rho\mathbf{v} \\ \rho\mathbf{v}\mathbf{v} + P\mathbf{I} \\ (\rho E + P)\mathbf{v} \end{pmatrix} \quad \mathbf{D} = \begin{pmatrix} 0 \\ \tau \\ \lambda\nabla T + \tau\cdot\mathbf{v} \end{pmatrix} \quad \mathbf{S} = \begin{pmatrix} 0 \\ \mathcal{S} \\ \mathcal{Q} + \mathbf{v}\cdot\mathcal{S} \end{pmatrix},$$

$$\langle \mathcal{S}_{ij}(\mathbf{r},t)\mathcal{S}_{k\ell}(\mathbf{r}',t')\rangle = 2k_B\eta T\left(\delta^K_{ik}\delta^K_{j\ell} + \delta^K_{i\ell}\delta^K_{jk} - \tfrac{2}{3}\delta^K_{ij}\delta^K_{k\ell}\right)\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'),$$

$$\langle \mathcal{Q}_i(\mathbf{r},t)\mathcal{Q}_j(\mathbf{r}',t')\rangle = 2k_B\lambda T^2\delta^K_{ij}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'),$$

$$\tau = \eta(\nabla\mathbf{v} + (\nabla\mathbf{v})^T) - \frac{2}{3}\eta\,\mathbb{I}\,\nabla\cdot\mathbf{v}$$

Stochastic PDE's

Consider system of the form

$$d\mathcal{U} = \mathcal{L}\mathcal{U}dt + \mathcal{K}dB$$

where B a cylindrical Weiner process (dB is Gaussian random field)

We can characterize the solution of these types of equations in terms of the invariant distribution, given by the covariance

$$S(k,\omega) =< \widehat{\mathcal{U}}(k,\omega), \widehat{\mathcal{U}}^*(k,\omega) >$$

known as the dynamic structure factor

Fourier transform to obtain

$$i\omega\ d\widehat{\mathcal{U}} = \widehat{\mathcal{L}}\widehat{U}d\omega + \widehat{\mathcal{K}}d\widehat{B}$$

Then

$$S(k,\omega) = (\widehat{L} - i\omega)^{-1}(\widehat{K}\widehat{K}^*)(\widehat{L}^* + i\omega)^{-1}$$

We can also define the static structure factor

$$S(k) = \int_{-\infty}^{\infty} S(k,\omega)d\omega$$

Static structure factor characterizes fluctuation dissipation of SPDE system

Fluctuation dissipation relation – discrete form

For

$$\partial_t U = AU + LU + KZ \quad \text{where} \qquad A = -A^* \quad \text{and} \qquad L = L^*$$

if

$$2\gamma L = -KK^*$$

then the equation satisfies a fluctuation dissipation relation with

$$S(k) = 2\gamma I \quad ,$$

which mimics the analytical form $\gamma(\mathcal{L} + \mathcal{L}^*) = -\mathcal{K}\mathcal{K}^*$

Would like to construct numerics so that

$$S^{num}(k) = 2\gamma(1 + \alpha k^{2p})$$

for small k and

$$S^{num}(k) \leq 2\gamma(1{+}???) \quad \text{forall } k.$$

Want approximations to differential operators with these properties discretely.

Spatial approximation

Consider finite volume discretizations where u_j^n represents average value of solution on the j^{th} cell at time t^n.

Define a discrete divergence that approximates cell-center divergence of a field defined at cell edges

$$(DF)_j = \frac{F_{j+1/2} - F_{j-1/2}}{\Delta x}$$

The adjoint to D then defines a discrete gradient at cell edges from values defined a cell centers

$$-(Gv)_{j+1/2} = (D^T v)_{j+1/2} = \frac{v_{j+1} - v_j}{\Delta x}$$

Then DG defines a cell-centered Laplacian L with $2L = -\sqrt{2}D(\sqrt(2)D)^T$.

Centered approximation of advection

We will also approximate the noise by

$$\mathcal{Z} = \frac{Z^n_{j+1/2}}{\sqrt{\Delta t V_c}}$$

where $Z^n_{j+1/2}$ is a normally distributed random variable and the scale approximates a δ function in space and time

RK3

We consider an alternative Runge Kutta scheme for stochastic systems $U_t = R(U, W)$

$$
\begin{aligned}
U_{i,j,k}^{n+1/3} &= U_{i,j,k}^{n} + \Delta t \mathbf{R}(U^n, W_1) \\
U_{i,j,k}^{n+2/3} &= \frac{3}{4} U_{i,j,k}^{n} + \frac{1}{4}\left[U_{i,j,k}^{n+1/3} + \Delta t \mathbf{R}(U^{n+\frac{1}{3}}, W_2)\right] \\
U_{i,j,k}^{n+1} &= \frac{1}{3} U_{i,j,k}^{n} + \frac{2}{3}\left[U_{i,j,k}^{n+2/3} + \Delta t \mathbf{R}(U^{n+\frac{2}{3}}, W_3)\right]
\end{aligned}
$$

W_i denote the random fields used in each stage of the integration.

We generate two sets of normally distributed independent Gaussian fields, W^A and W^B, and set

$$
\begin{aligned}
W_1 &= Z^A + \beta_1 Z^B \\
W_2 &= Z^A + \beta_2 Z^B \\
W_3 &= Z^A + \beta_3 Z^B
\end{aligned}
$$

where $\beta_1 = (2\sqrt{2} + \sqrt{3})/5$, $\beta_2 = (-4\sqrt{2} + 3\sqrt{3})/5$, and $\beta_3 = (\sqrt{2} - 2\sqrt{3})/10$.

The RK3 scheme has good stability properties, is weakly second-order accurate.

Multidimensional considerations

Standard discretizations of stress tensor in fully cell-centered finite volume approach leads to velocity correlations – can't compute divergence of stochastics stress in a way that is consistent with symmetrized gradient of velocity

$$\tau = \eta(\nabla U + (\nabla U)^T) - \frac{2}{3}\eta \mathbb{I} \nabla \cdot U$$

Rewrite stress tensor as

$$\nabla \cdot (\eta(\nabla U + (\nabla U)^T) - \frac{2}{3}\nabla \cdot (\eta \nabla \cdot U \, \mathbb{I}) = \nabla \cdot \eta \nabla U + \frac{1}{3}\nabla \cdot (\eta \mathbb{I} \, \nabla \cdot U) + \mathrm{cross} - \mathrm{terms}$$

Generate noise for first term at edges and noise for second term at corners

Cross terms included in deterministic discretization but no corresponding noise.

Alternative approach based on staggered grid approximation

- Easier to construct scheme with desired discrete fluctuation dissipation relation
- Harder to construct a hybrid discretization
- Balboa *et al.*

Multicomponent flow equations

Starting point is deterministic multicomponent flow equations

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

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

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

Augment deterministic fluxes with stochastic fluxes to represent fluctuations

Curie priniciple $\rightarrow$ stochastic stress tensor unchanged from single component equations

What is the noise in the energy and species equations?

Entropy production

Entropy production given by

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

where

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

and

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

General form of the phenomenological laws writes fluxes as sums of thermodynamics forces

$$\mathbf{J} = \mathfrak{L}\mathbf{X} \qquad \text{where} \qquad \mathfrak{v} = \mathbf{J}^T\mathbf{X} = \mathbf{X}^T\mathfrak{L}^T\mathbf{X}.$$

with

$$\mathbf{J} = \begin{bmatrix}\boldsymbol{\mathcal{F}}\\ \boldsymbol{\mathcal{Q}}'\end{bmatrix} \qquad \text{and} \qquad \mathbf{X} = \begin{bmatrix}-\frac{1}{T}\nabla_T\mu_i\\ -\frac{1}{T^2}\nabla T\end{bmatrix}$$

Fluctuation dissipation

Onsager reciprocity says $\mathfrak{L}$ is symmetric so

$$\mathfrak{L} = \begin{bmatrix} \mathbf{L} & \mathbf{L}\xi \\ \xi^T \mathbf{L} & \zeta + \xi^T \mathbf{L} \xi \end{bmatrix} \quad .$$

Here L is rank deficient of the form

$$\mathbf{L} = \begin{bmatrix} \hat{\mathbf{L}} & -\hat{\mathbf{L}} e \\ -e^T \hat{\mathbf{L}} & e^T \hat{\mathbf{L}} e \end{bmatrix}$$

Similarly, $e^T \xi = 0$. If we define the stochastic fluxes

$$\widetilde{\mathbf{J}}_\alpha = \begin{bmatrix} \widetilde{\boldsymbol{\mathcal{F}}}_\alpha \\ \widetilde{\boldsymbol{\mathcal{Q}}}'_\alpha \end{bmatrix}$$

then from fluctuation dissipation balance, the fluxes are white in space and time with a correlation matrix given by

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

Stochastic fluxes

Stochastic fluxes are not uniquely determined. Require noise terms with correct covariance

Use Cholesky factorization of $\mathfrak{L}$; i.e., $\mathcal{B}\mathcal{B}^T = 2k_b\mathfrak{L}$

$$\tilde{\mathbf{J}}_\alpha = \mathcal{B}\mathbf{W}^{(\alpha)} \qquad \text{where} \qquad \mathbf{W}^{(\alpha)} = \begin{bmatrix} W^{(\boldsymbol{\mathcal{F}};\alpha)} \\ \mathcal{W}^{(\boldsymbol{\mathcal{Q}}';\alpha)} \end{bmatrix}$$

where the noise amplitude matrix $\mathcal{B}$ can be written as,

$$\mathcal{B} = \begin{bmatrix} \mathbf{B} & 0 \\ \xi^T\mathbf{B} & \sqrt{\zeta} \end{bmatrix}$$

For $\mathcal{B}$ to have the correct covariance, we require that $\mathbf{B}\mathbf{B}^T = 2k_B\mathbf{L}$
Stochastic fluxes are then

$$\widetilde{\boldsymbol{\mathcal{F}}}_\alpha = \mathbf{B}\mathcal{Z}^{\boldsymbol{\mathcal{F}};\alpha} \qquad \widetilde{\boldsymbol{\mathcal{Q}}}_\alpha = \sqrt{\zeta}\mathcal{Z}^{\boldsymbol{\mathcal{Q}}';\alpha} + (\mathbf{h}^T + \xi^T)\widetilde{\boldsymbol{\mathcal{F}}}_\alpha$$

Ideal gas mixtures

For an ideal gas mixture, chemical potential is of the form

$$\mu_i = \frac{R_u T}{W_i} \ln(\frac{X_i p}{p_{st}}) + f(T)$$

Substituting into above general formalism establishes correspondence between transport model used in continuum modeling and nonequilibrium thermodynamic framework

Link to EGLIB package of Ern and Giovangigli

Direct correspondence with GENERIC framework of Ottinger

For systems written in terms of matrix of diffusion coefficients $D \times$ gradients of mole fractions and pressure

$$\mathbf{L} \approx D \left[\frac{\partial \mu}{\partial X} \right]^{-1}$$

and

$$\mathbf{L} \frac{\partial \mu}{\partial p}$$

is the barodiffusion coefficient

Equilibrium fluctuations

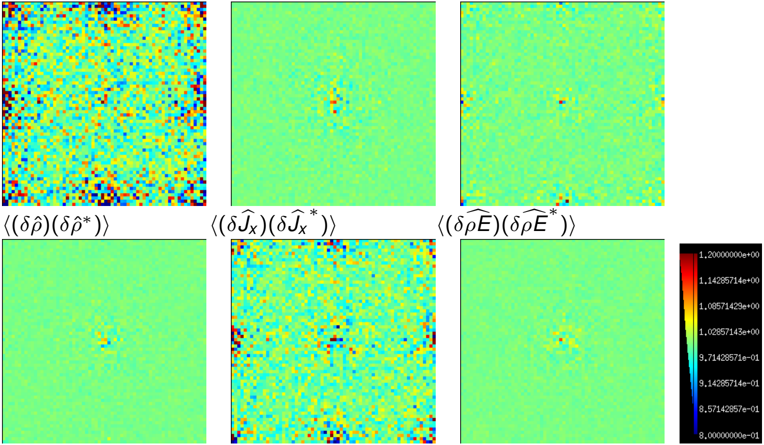
Hard sphere model of noble gases

k	Species	Molecular Weight	Diameter (cm)	Y_k	X_k
1	Helium	4.0026	2.18×10^{-8}	0.25	0.7428
2	Neon	20.1797	2.58×10^{-8}	0.25	0.1473
3	Argon	39.9480	3.63×10^{-8}	0.25	0.0744
4	Krypton	83.8000	4.16×10^{-8}	0.25	0.0355

$p = 1\text{atm}$, $T = 300\text{K}$

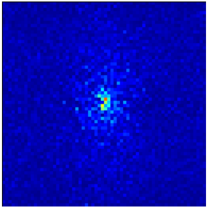
64^3 mesh with $h = 8 \times 10^{-6}\text{cm}$, $\Delta t = 10^{-12}$

Static structure factors – Variances

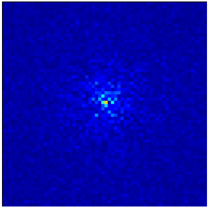


$\langle(\delta\hat{\rho})(\delta\hat{\rho}^*)\rangle$ $\langle(\delta\widehat{J_x})(\delta\widehat{J_x}^*)\rangle$ $\langle(\delta\widehat{\rho E})(\delta\widehat{\rho E}^*)\rangle$

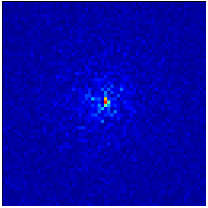
$\langle(\delta\hat{\rho}_1)(\delta\hat{\rho}_1{}^*)\rangle$ $\langle(\delta\hat{\rho}_4)(\delta\hat{\rho}_4{}^*)\rangle$ $\langle(\delta\hat{T})(\delta\hat{T}^*)\rangle$



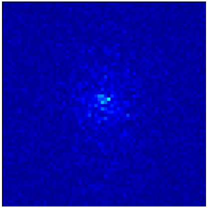
$|\langle(\delta\hat{\rho})(\delta\widehat{J_x}^{\,*})\rangle|$



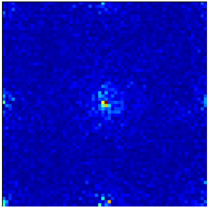
$|\langle(\delta\hat{\rho})(\delta\hat{T}^*)\rangle|$



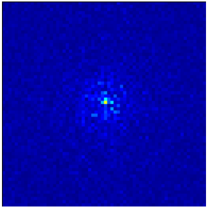
$|\langle(\delta\widehat{J_x})(\delta\widehat{J_y}^{\,*})\rangle|$



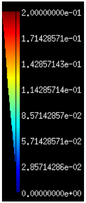
$|\langle(\delta\widehat{J_x})(\delta\widehat{\rho E}^{\,*})\rangle|$



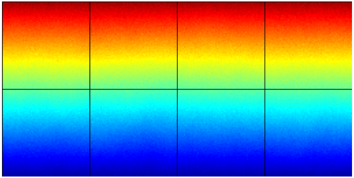
$|\langle(\delta\hat{\rho}_1)(\delta\hat{\rho}_4^*)\rangle|$



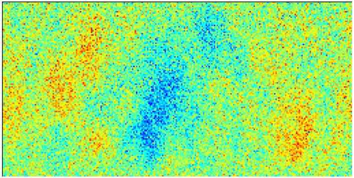
$|\langle(\delta\widehat{v_x})(\delta\hat{T}^*)\rangle|$



Nonequilibrium – diffusion barrier



Mole fraction of red particle



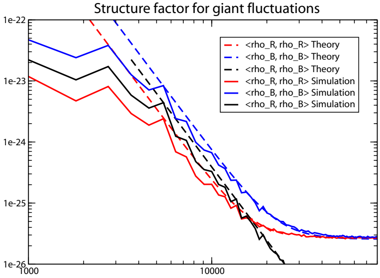
Fluctuations obtained by subtracting horizontal average

Equal mass particles, R, B, G. G has large diameter

$dY_R/dy = 28.935$, $dY_B/dy = 90.760$ and $dY_G/dy = -119.695$

Deterministic flux of red particles is zero.

Theory for spectrum of long-range correlations due to nonequilibrium conditions



Current research directions

Physics

- Reactions
- Phase transition phenomena
- Non-ideal fluid effects

Numerical models

- Incompressible flow models
- Generalized low Mach number models
- Semi-implicit time-stepping schemes

Reacting systems

Extend multicomponent FNS solver to reacting systems

Species equations are given by

$$\frac{\partial}{\partial t}(\rho Y_k) + \nabla \cdot (\rho U Y_k) + \nabla \cdot \left[F_k + \widetilde{F_k}\right] = \rho\left[\omega_k + \widetilde{\omega_k}\right]$$

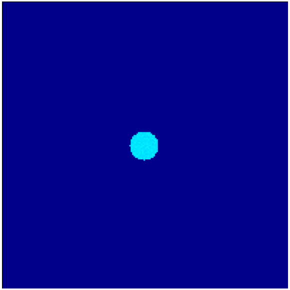
Stochastic reaction models

- "Standard" chemical Langevin model
- Master equation approach
- Alternative forms of chemical Langevin better suited for systems far from equilibrium

Reactions in fluctuating systems

Investigate effect of fluctuations on Turing instability pattern formation resulting

$$\begin{aligned} A &\xrightarrow{k_1} C, \\ 2A + B &\xrightarrow{k_2} 3A, \\ B &\xrightarrow{k_3} D, \\ D &\xrightarrow{k_4} B, \end{aligned}$$



with D held fixed

System admits homogeneous steady states

$$(A_0, B_0, C_0, D_0)\,, \qquad (A_+, B_+, C_+, D_+)\,, \qquad (A_-, B_-, C_-, D_-)$$

A small region at the state $+$, when exposed to a surrounding large region at state 0, gives rise to an evolving chemical wave front.

Turing instability ensues, giving rise to pattern formation

Gas-liquid phase transitions

van der Waals model

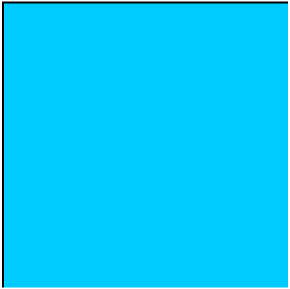
- Mean-field theory for hard spheres with long-range attractive interaction
- Simple model for liquid-gas transitions in one-component fluids
- Add gradient term for Helmholtz free energy

$$\frac{\kappa}{2}|\nabla\rho|^2$$

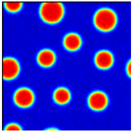
Results in a regularizing stress term added to the continuum equations representing interfacial tension

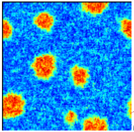
$$\kappa[\rho\nabla^2\rho + \frac{|\nabla\rho|^2}{2} - \frac{\rho}{T}\nabla\rho\cdot\nabla T]\mathbb{I} - \kappa\nabla\rho\otimes\nabla\rho$$

Fluctuating terms unchanged . . . no entropy production associated with interfacial tension



Higher noise accelerates merger events





Low Mach number systems

Isothermal, low Mach number systems: incompressible fluids of different densities with no volume change on mixing

$$\text{EOS}: \quad \frac{1}{\rho} = \frac{\mathrm{c}}{\rho_1} + \frac{1-\mathrm{c}}{\rho_2}$$

Gives system of the form

$$\rho_t + \nabla \cdot \rho U = 0$$

$$(\rho U)_t = -\nabla\pi - \nabla \cdot (\rho U U) + \nu \Delta U + \nabla \cdot \sqrt{2\nu\rho k_B T}\, W_v$$

$$(\rho c)_t = -\nabla \cdot (\rho U c) + \nabla \cdot \rho\chi\nabla c + \nabla \cdot \sqrt{2\chi\rho M c(1-c)}\, W_c$$

Differentiation of equation of state gives

$$\nabla \cdot U = -\frac{1}{\rho}\frac{\partial \rho}{\partial c}(\nabla \cdot \rho\chi\nabla c + \nabla \cdot \sqrt{2\chi\rho M c(1-c)}\, W_c)$$

Structure factor modified by projection

- Numerics based on method of lines approach using gauge ideas
- Need discretely idempotent projection – staggered grid
- Need to avoid commuting projection with diffusion – Stokes solver

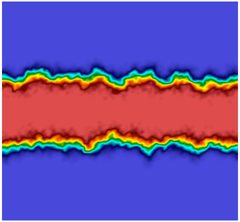
Comparison to MD simulation

Models can be validated against theory in a variety of equilibrium and non-equilibrium settings

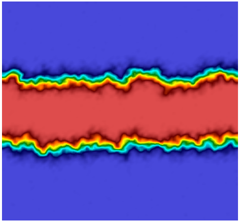
Direct comparison with particle models

Molecular dynamics

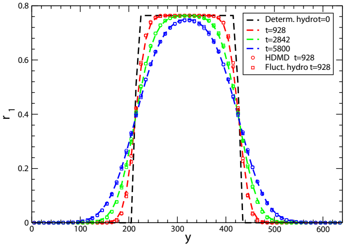
- Two-dimensional hard-disk fluid
- 128 x 128 hydrodynamics cells
- 1.25 million disks
- Average ensemble to compute effective mixing



Molecular Dynamics

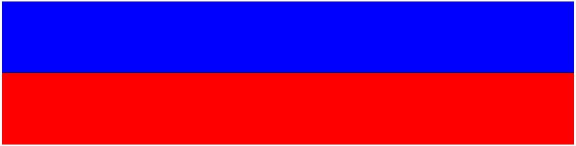


Fluctuating Navier Stokes



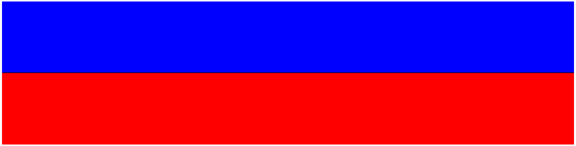
Essemble / horizontal average

Low Mach number solver



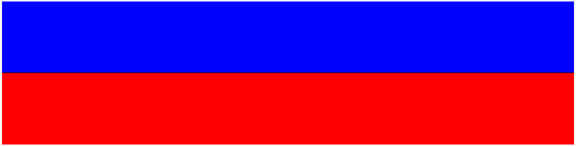
No gravity

$\rho_2/\rho_1 = 5/3$



Gravity

$\rho_2/\rho_1 = 5/3$



No gravity

$\rho_2/\rho_1 = 10$

Summary

Numerical methodology for multicomponent fluctuating hydrodynamics

- Generic FNS formulation
- Specialized to ideal gas mixtures
- RK3 centered scheme
- Designed to satisfy discrete fluctuation dissipation balance
- Give correct equilibrium fluctuations

Future / current directions

- Reacting systems
- Complex fluids
- Low Mach number versions

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