# Fluctuating Hydrodynamics for Transport in Neutral and Charged Fluid Mixtures

Alejandro L. Garcia

*San Jose State University*

*Lawrence Berkeley Nat. Lab.*

Hydrodynamic Fluctuations in Soft Matter Simulations
February 9-12, 2016
Monash University Prato Centre, Italy

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# Credits

**Berkeley Lab**
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K. Balakrishnan
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**Courant Institute**
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Y. Sun

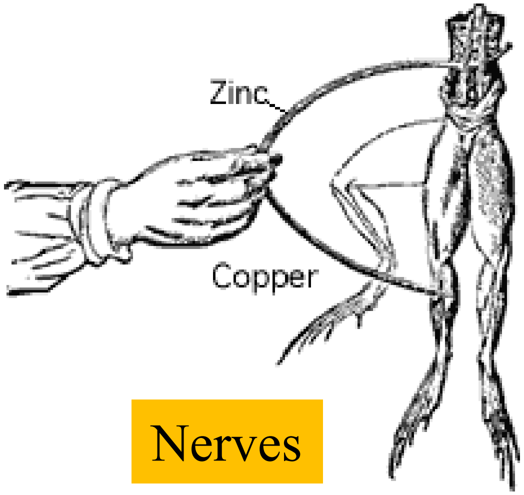
Supported by DoE

For more information,
visit: ccse.lbl.gov
and cims.nyu.edu/~donev

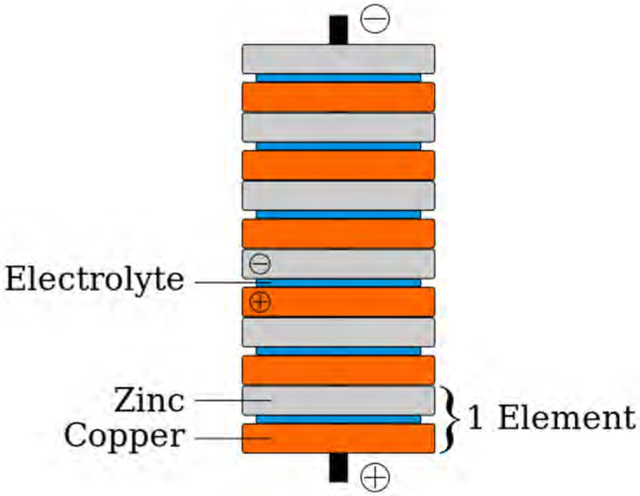
# Electrolytes

Scientists first became interested in electrolytes after Volta’s discoveries.

Alessandro Volta explains the battery to Napoleon in 1801

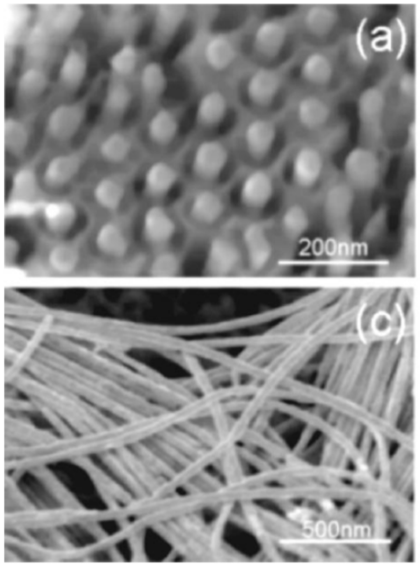


Nerves



Voltaic pile

# Electrolytes



Nanowires made by electrodeposition

Electrolyte Applications
- * Energy technology (e.g., Batteries, Fuel Cells)
- * Fabrication (e.g., Electrodeposition)
- * Cellular biology (e.g., Nerve Cells)

Types of Electrolytes
Solutions, Molten salts, Gels, Solids, Gases (Plasma)

Microscopic theories date back to 1884 when Arrhenius, in his doctoral thesis, correctly identified the role of ions in solutions. This work led to his Nobel in Chemistry (1903) .

# Outline of the Talk

Fluctuating hydrodynamics for multi-species transport

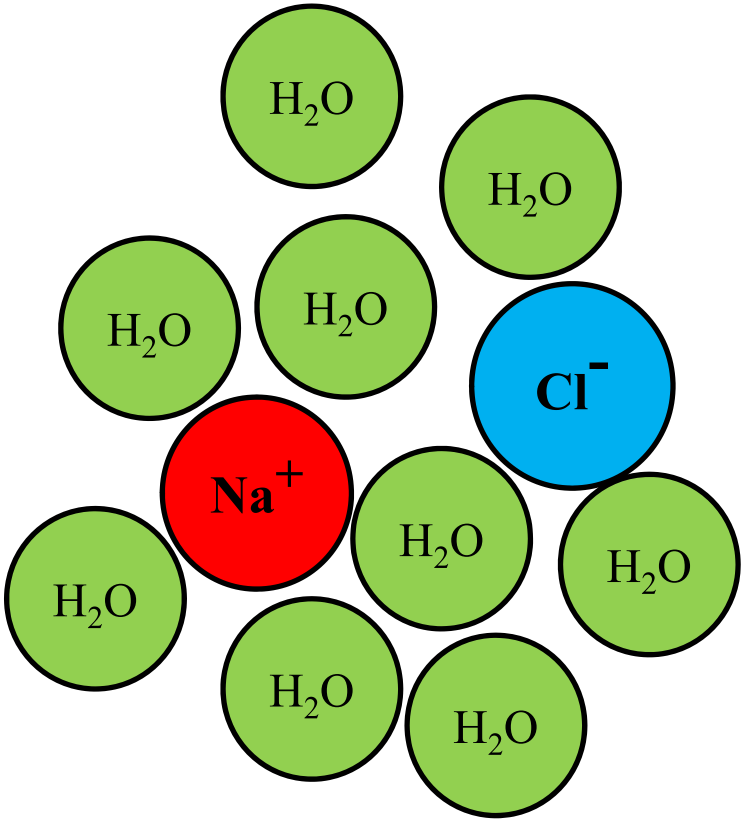
Neutral species mixtures
- Theory
- Numerics
- Examples

*A. Donev, A. Nonaka, A. Bhattacharjee, ALG, and, J.B. Bell, *Phys. Fluids* **27** 037103 (2015).
*K. Balakrishnan, ALG, A. Donev, and J.B. Bell, *Physical Review E* 89 013017 (2014).
*A. Donev, A. J. Nonaka, Y. Sun, T. Fai, ALG, and J. B. Bell, *Comm. Applied Math.* Comp. Sci., **9** 47 (2014).

Charged species mixtures
- Theory
- Numerics
- Examples

Preliminary results

# Multispecies Mixtures



No distinction between solvent and solute species.

Model an electrolyte at the hydrodynamic level:

* $\rho_k$ - Mass density of species $k$
* $\mathbf{v}$ - Fluid velocity
* $T$ - Temperature

Also need thermodynamic properties (equation of state, chemical potential, etc.) and transport coefficients (viscosity, diffusion coefficient, etc.)

# Transport for Neutral Species

Hydrodynamic equation for the mass densities, $\rho_k$, for species $k$ has the form,

$$\partial_t \rho_k = -\nabla \cdot (\rho_k \boldsymbol{v}) - \nabla \cdot \boldsymbol{F}_k \qquad\qquad k = 1, \ldots, N$$

where the species flux, $\boldsymbol{F}_k$, is the sum of a deterministic plus a stochastic contribution,

$$\boldsymbol{F}_k = \overline{\boldsymbol{F}_k} + \widetilde{\boldsymbol{F}_k}$$

Note that by mass conservation,

$$\sum_k \boldsymbol{F}_k = 0 \qquad \text{so} \qquad \partial_t \rho = -\nabla \cdot (\rho \boldsymbol{v})$$

# Deterministic Species Flux

In Fickian form the deterministic species flux is,

$$\overline{\boldsymbol{F}}_k = -\rho_k \sum_j^N \chi_{kj} \left( \boldsymbol{d}_j + \zeta_j \frac{\nabla T}{T} \right)$$

Diffusion Coefficients

Thermal Diffusion term

where the diffusion driving force, ***d***, is

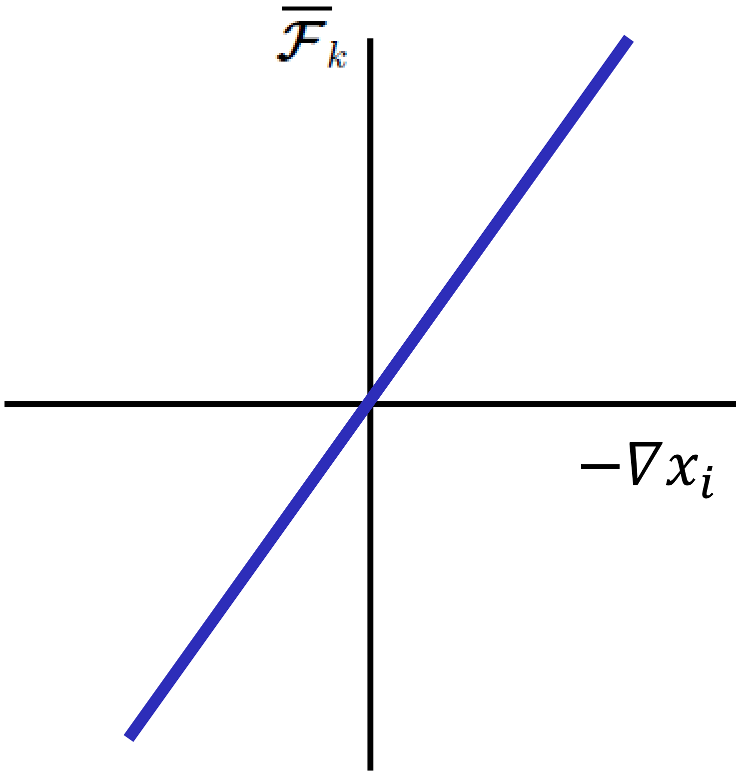
$$\boldsymbol{d}_j = \sum_i^N \Gamma_{ji} \nabla x_i + \frac{\bar{m}\phi_j}{\rho k_B T} \nabla p$$

Concentration Gradient term

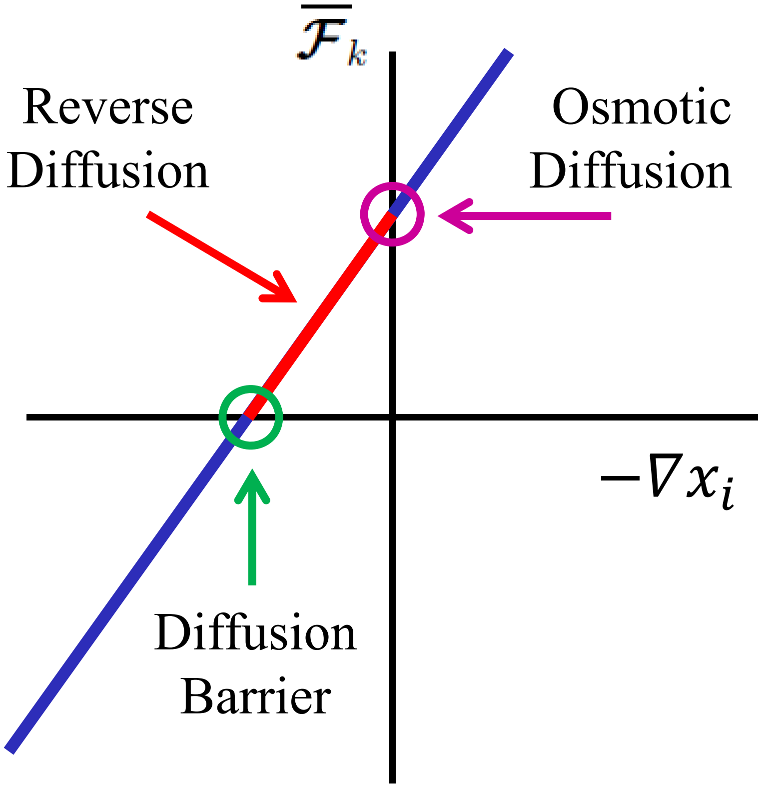
Barodiffusion term

Note that ***d*** has only thermodynamic quantities (i.e., no transport coefficients)

# Diffusion Interaction Effects



Binary Diffusion:
One Coefficient

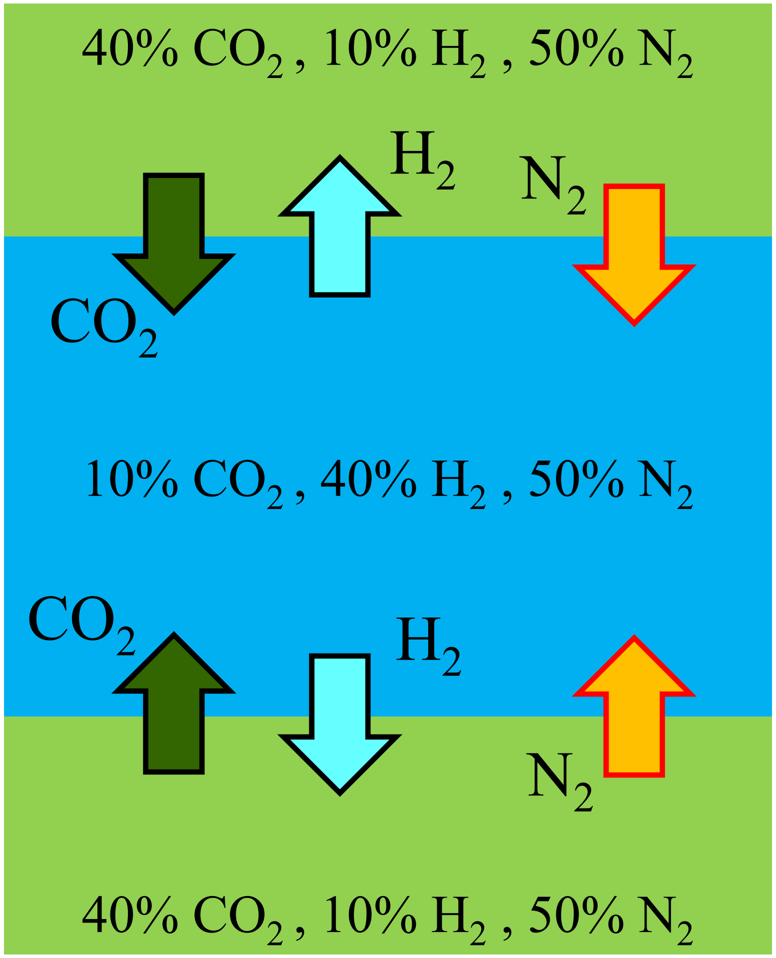


Ternary Diffusion:
Three Coefficients

# 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.

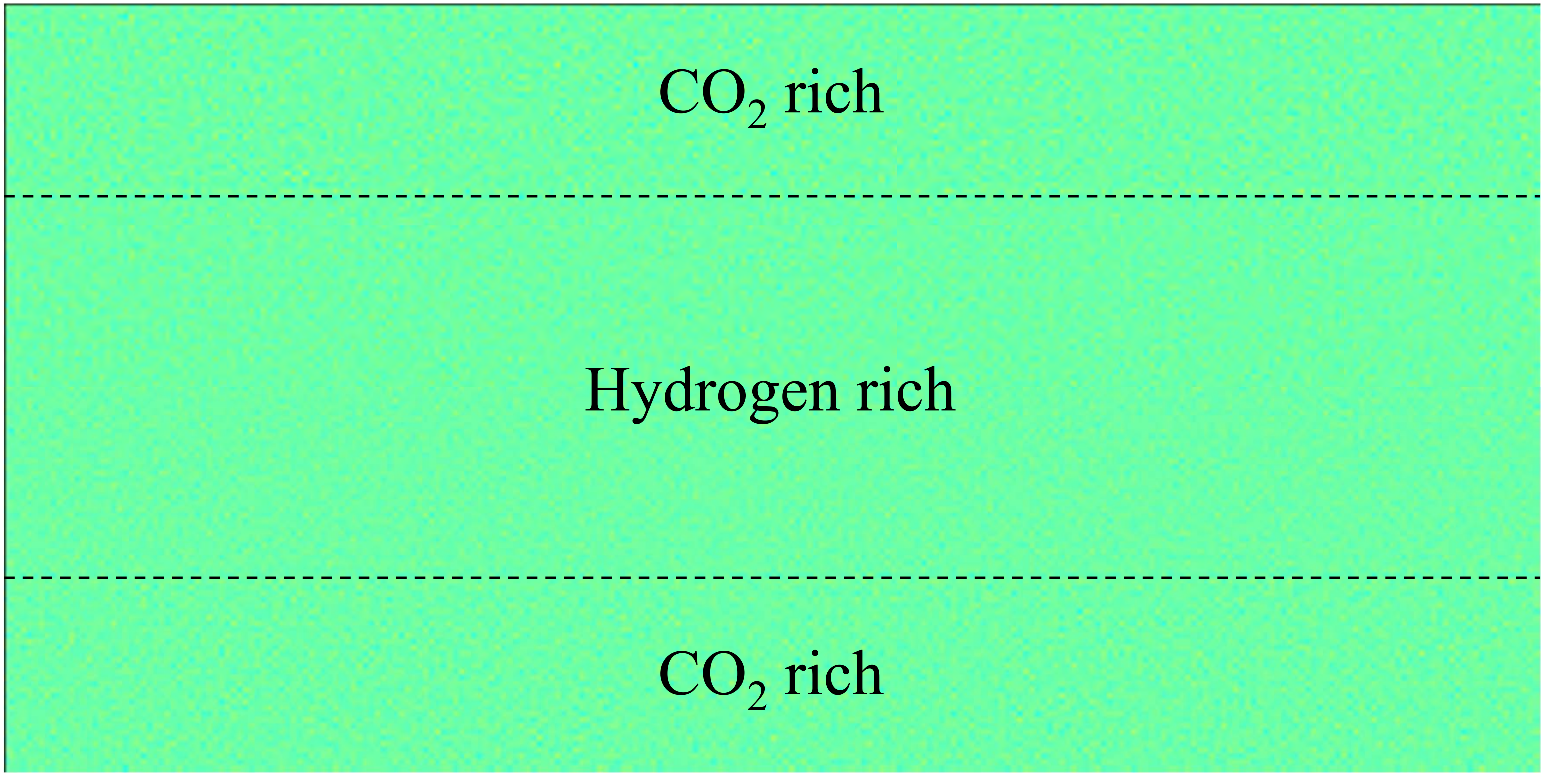
Duncan and Toor, *AIChE J.*, **8** 38-41 (1962)



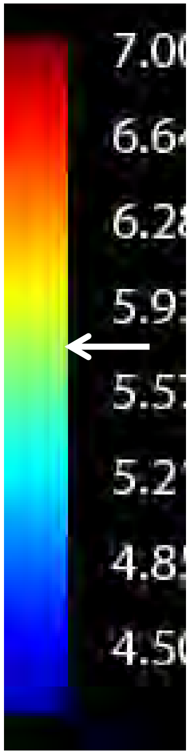
No gravity

# Reverse Diffusion Example

Nitrogen density is initially uniform but it becomes non-uniform due to the diffusion of the other two species.



Nitrogen Density



Initial nitrogen density = 5.7

Confirmed by laboratory experiments

# Onsager form

The deterministic species flux may also be written as,

$$\overline{\boldsymbol{F}_k} = -\frac{1}{T}\sum_{j}^{N} L_{kj}\left(\nabla_T \mu_j + \xi_j \frac{\nabla T}{T}\right)$$

Onsager Coefficients

where the gradient of chemical potential at constant *T* is,

$$\nabla_T \mu_j(\{x_i\}, p, T) = \sum_{i}^{N}\left(\frac{\partial \mu_i}{\partial x_i}\right)\nabla x_i + \left(\frac{\partial \mu_j}{\partial p}\right)\nabla p$$

We may match the transport coefficients in the Fickian form to the coefficients in the Onsager form.

# Stochastic Species Flux

The matrix of Onsager coefficients, $\boldsymbol{L}$, is related to the matrix of diffusion coefficients, $\boldsymbol{\chi}$, as,

$$L_{kj} = \frac{\bar{m}}{\rho k_B}\rho_k \rho_j \chi_{kj}$$

By fluctuation-dissipation the stochastic species flus is,

$$\widetilde{\boldsymbol{F}_k} = \sqrt{2k_B}\sum_j^N \underset{\substack{\uparrow \\ \text{Matrix “square root”}}}{[\boldsymbol{L}^{1/2}]}_{kj}\; \underset{\substack{\uparrow \\ \text{White noise}}}{\mathbb{Z}_j}$$

Get $\boldsymbol{L}^{1/2}$ by Cholesky decomposition of $\boldsymbol{\chi}$.

# Chemistry

Chemistry can also be included as a stochastic source term,

$$\partial_t \rho_k = -\nabla \cdot (\rho_k \boldsymbol{v}) - \nabla \cdot F_k + m_k \Omega_k$$

For example, for the simple dimerization reaction,

$$A + A \rightleftharpoons A_2$$

By the law of mass action and using the chemical Langevin equation the deterministic and stochastic production rates for the monomer species are,

$$\overline{\Omega}_1 = -2k^+ n_1^2 + 2k^- n_2 \qquad \widetilde{\Omega}_1 = 2\sqrt{k^+ n_1^2 + k^- n_2}\,\mathbb{Z}$$

# Momentum Equation

The general form of the momentum equation is

$$\partial_t(\rho\boldsymbol{v}) = -\nabla\cdot(\rho\boldsymbol{v}\boldsymbol{v}^T) - \nabla p - \nabla\cdot\boldsymbol{\Pi} + \rho\boldsymbol{g}$$

The stress tensor is $\boldsymbol{\Pi} = \overline{\boldsymbol{\Pi}} + \widetilde{\boldsymbol{\Pi}}$

$$\overline{\boldsymbol{\Pi}} = -\eta(\nabla\boldsymbol{v} + \nabla\boldsymbol{v}^T) - \left(\kappa - \tfrac{2}{3}\eta\right)\boldsymbol{I}(\nabla\cdot\boldsymbol{v})$$

$$\widetilde{\boldsymbol{\Pi}} = \sqrt{2k_BT\eta}\,\breve{\mathbb{Z}} + \left(\sqrt{\frac{k_B\eta_bT}{3}} - \sqrt{\frac{2k_B\eta T}{3}}\right)\mathrm{Trace}(\breve{\mathbb{Z}})$$

where $\breve{\mathbb{Z}} = (\mathbb{Z} + \mathbb{Z}^T)/\sqrt{2}$

This is just a fancy way of writing what's given in Landau

# Low-Mach Approximation

In the low-Mach approximation we write,

$$\partial_t(\rho\boldsymbol{v}) = -\nabla\cdot(\rho\boldsymbol{v}\boldsymbol{v}^T) - \nabla\pi - \nabla\cdot\mathbf{\Pi} + \rho\boldsymbol{g}$$

and replace the equation of state with a constraint on the volume fraction, $\phi_k$, of the form,

**EOS Constraint**

$$\phi_k = \frac{\rho_k}{\overline{\rho_k}} \qquad \text{so} \qquad \sum_k^N \phi_k = \boxed{\sum_k^N \frac{\rho_k}{\overline{\rho_k}} = 1}$$

For example, for an ideal gas mixture at pressure $p_0$,

$$\phi_k = x_k \qquad \text{and} \qquad \overline{\rho_k} = \frac{m_k p_0}{k_B T}$$

Mole fraction

# Energy Equation

The hydrodynamic equation for energy density is,

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

Heat Flux

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

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

Note: In the low-Mach model we assume constant $T$.

# Numerics

The evolution equations for the species densities and fluid momentum are solved subject to the EOS constraint on the velocity field,

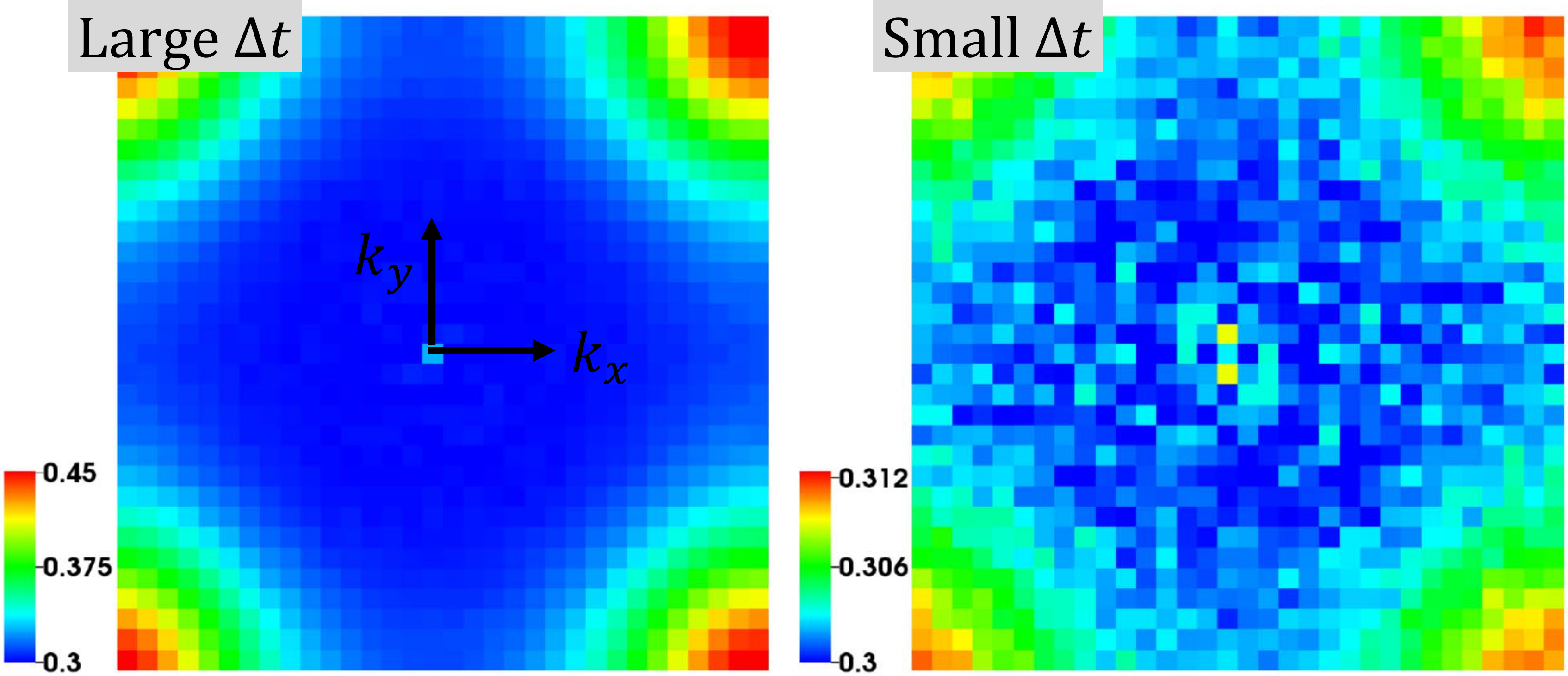
$$\nabla \cdot \boldsymbol{v} = -\nabla \cdot \left( \sum\nolimits_{k}^{N} \frac{1}{\overline{\rho_k}} \boldsymbol{F}_k \right)$$

We use a finite volume formulation over regular Cartesian cells to represent the cell-averaged density, and a staggered-grid formulation for face-averaged velocities.

A second-order predictor-corrector for density is used with a GMRES (Generalized minimal residual method) solver for the constrained velocity field evolution.

# Static Structure Factor

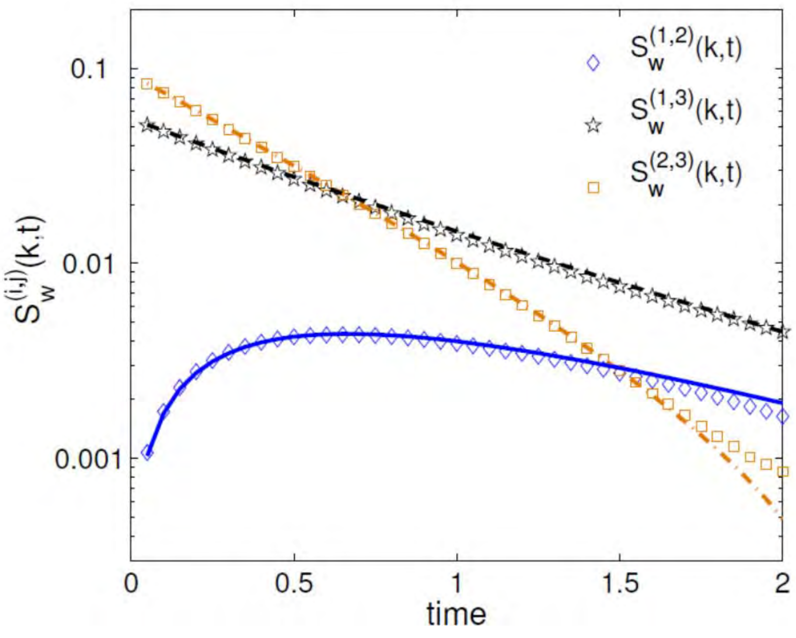
The simulations accurately reproduce the predicted constant equilibrium static structure factor for density fluctuations. This indicates that the fluctuation-dissipation is accurately simulated.

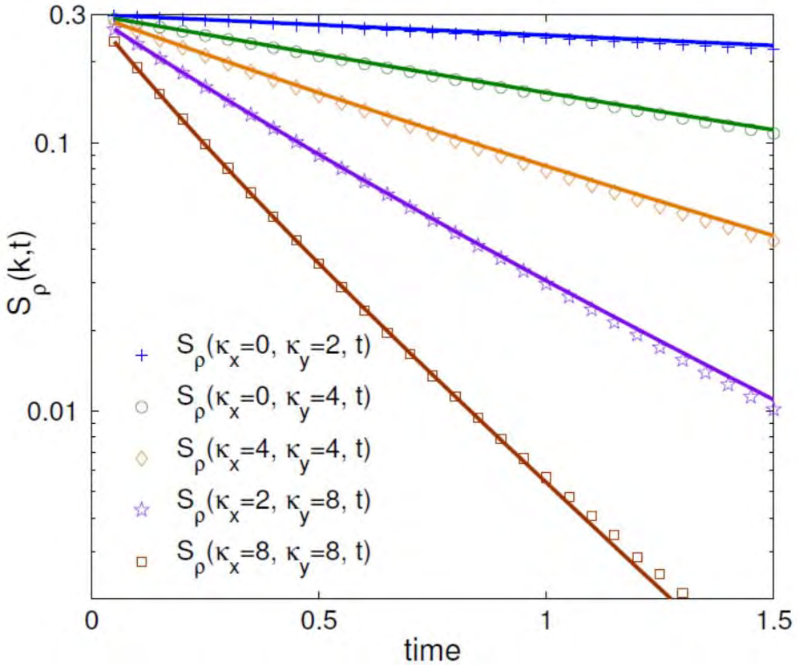


Correct result is 0.3 for all ***k*** values

# Dynamic Structure Factor

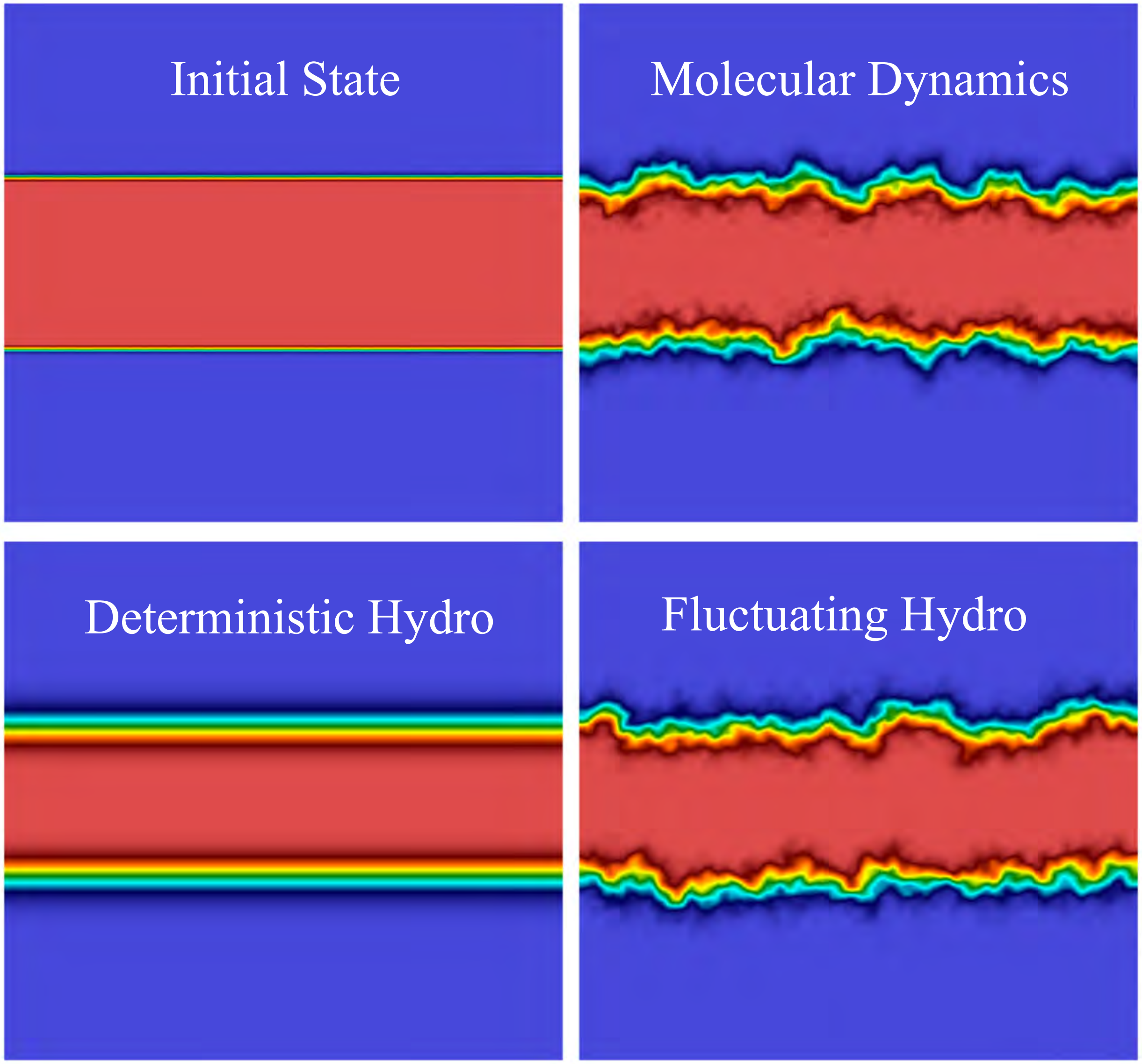
The simulations accurately reproduce the dynamic structure factor for concentration fluctuations as predicted by theory. This indicates that the transport is accurately simulated.





# Giant Fluctuations

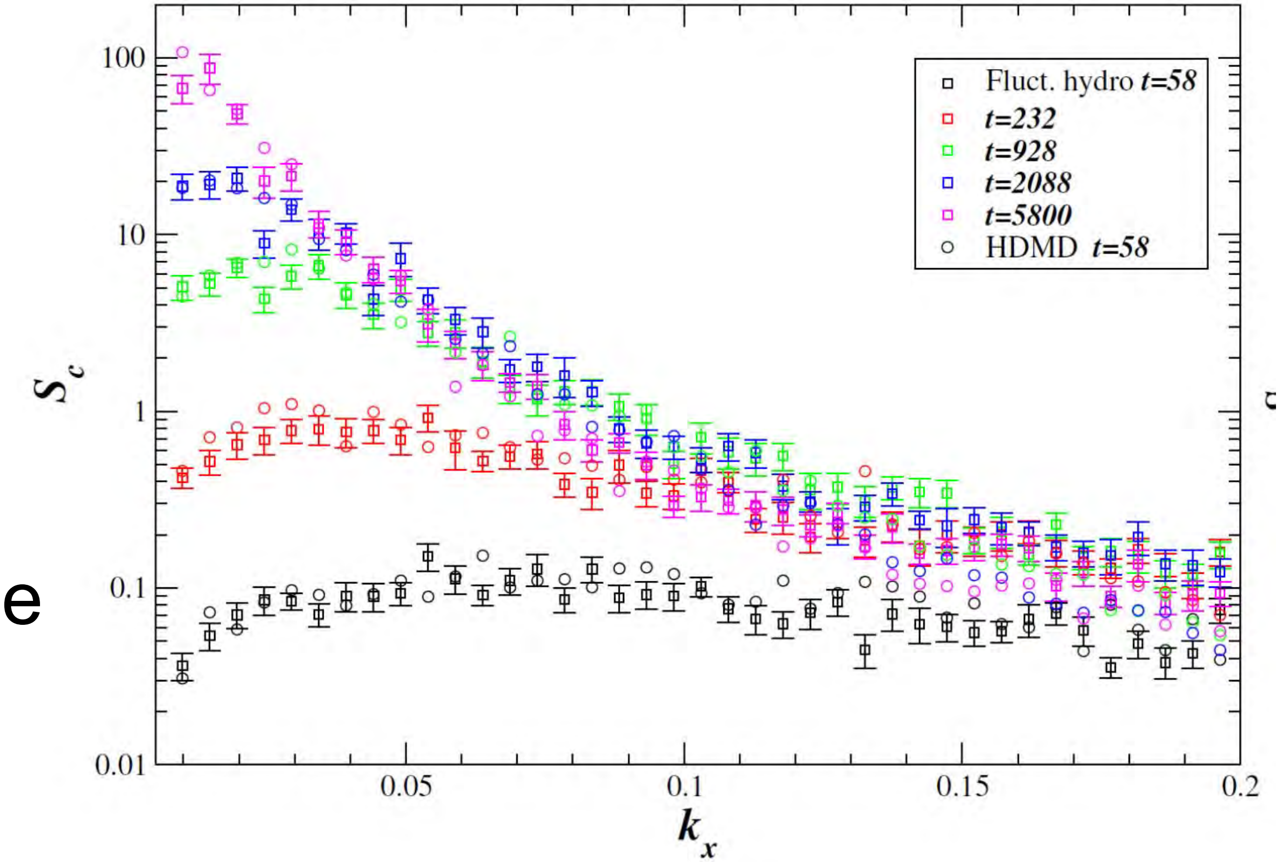
An interesting phenomena to investigate is the "giant fluctuations" effect due to correlation of concentration and velocity fluctuations.



# Giant Fluctuations

Excellent agreement of the molecular dynamics and fluctuating hydrodynamics simulations for the growth of the correlation of concentration fluctuations.

$$S_c = \langle \delta c(k_x) \delta c^*(k_x) \rangle$$

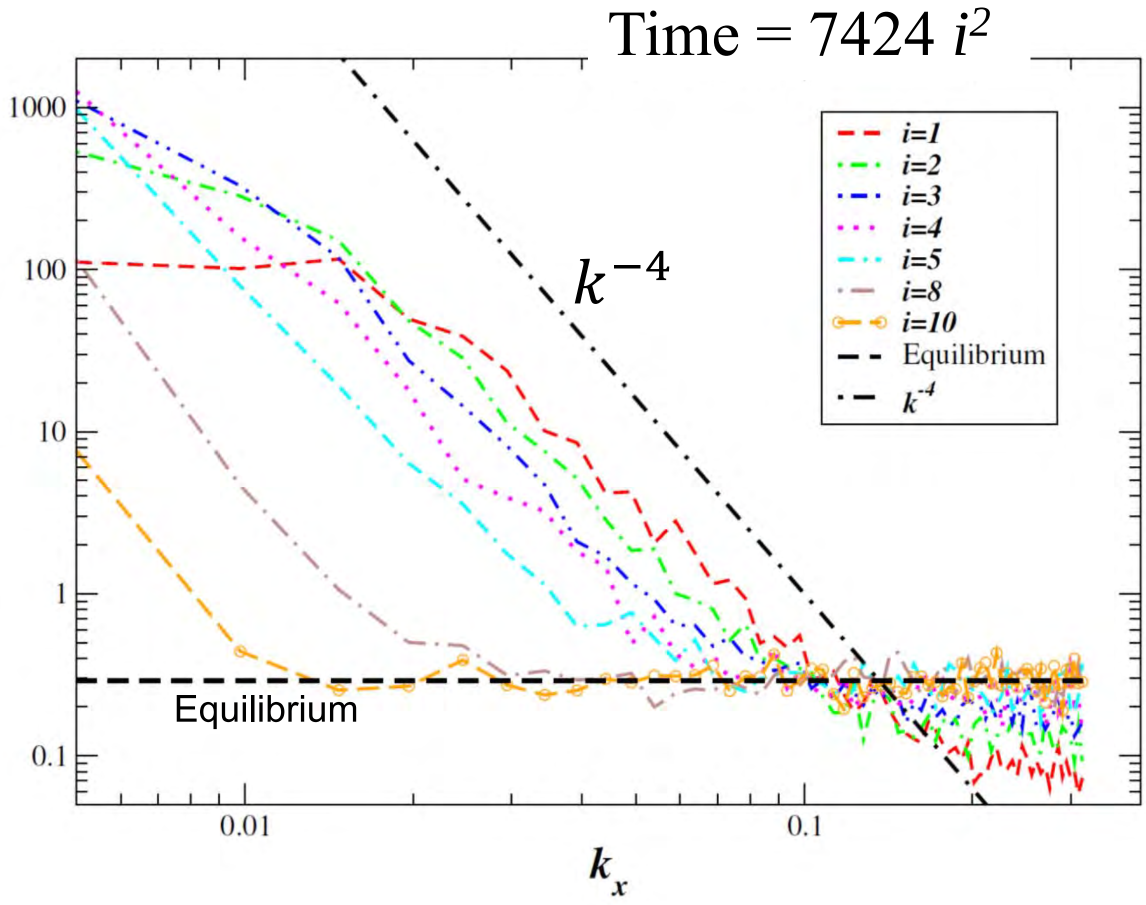


MD – Circles;  Fluct. Hydro. – Squares

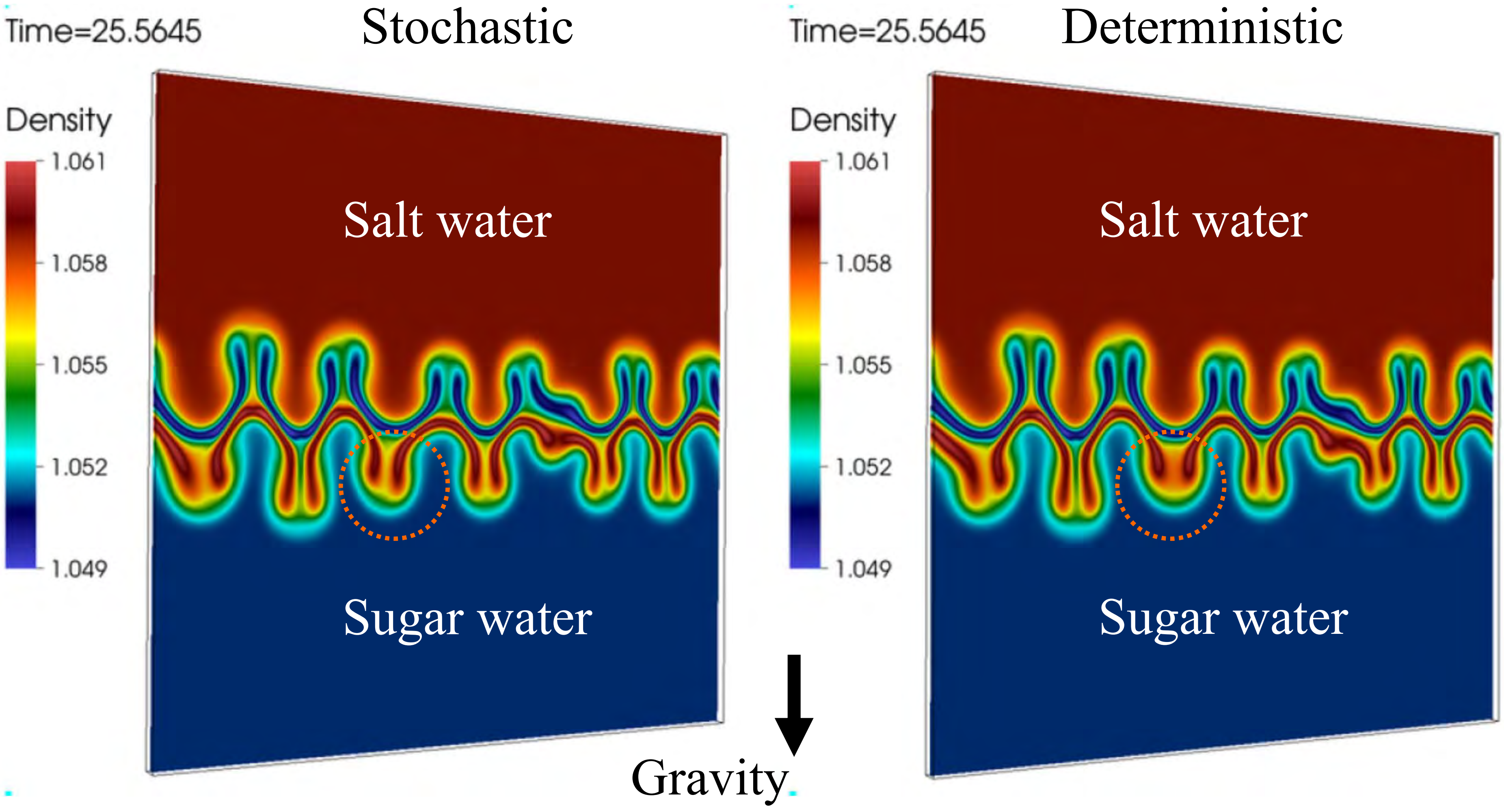
# Giant Fluctuations

At longer times MD simulations are not feasible but the fluctuating hydrodynamics simulations give good agreement with theory.

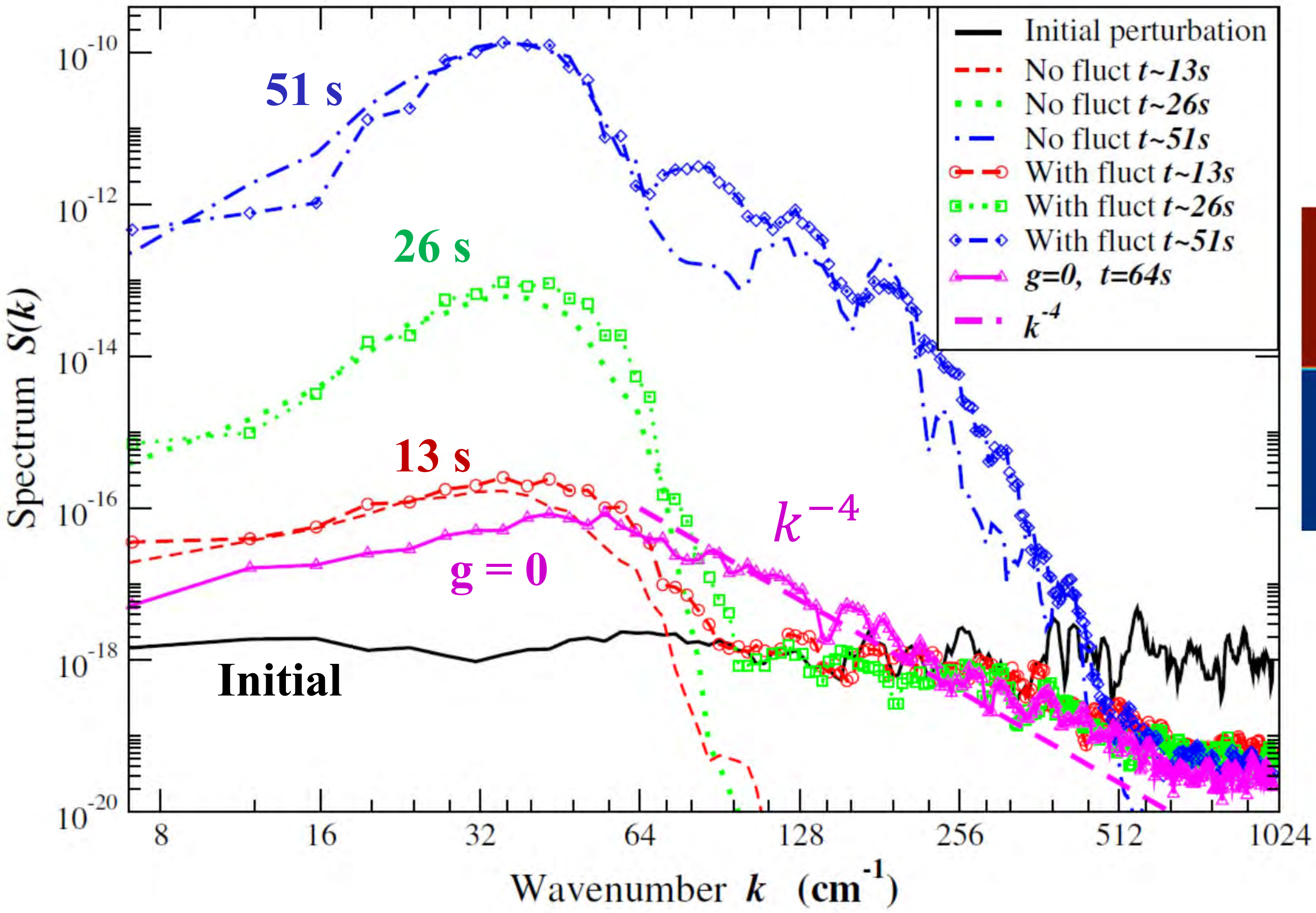
$$S_c \sim (\nabla c)^2\, k^{-4}$$

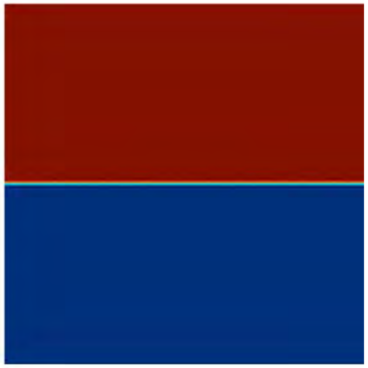


# Mixed-mode Instability



# Mixed-mode Instability





With gravity

# Electric Charge & Field

Define $z_k$ as the charge per unit mass so by Gauss's law,

$$\nabla \cdot (\epsilon \boldsymbol{E}) = -\nabla \cdot (\epsilon \nabla \Phi) = q = \sum_{k}^{N} \rho_k z_k$$

We assume constant permittivity so $-\epsilon \nabla^2 \Phi = q$.

With an electric field $\boldsymbol{E}$ the stress tensor has an additional contribution, the Maxwell stress tensor,

$$[\sigma]_{ij} = \epsilon E_i E_j - \frac{1}{2} \epsilon E^2 \delta_{ij}$$

which adds a Lorentz force, $-q\nabla\Phi$, to the momentum equation.

# Transport of Charged Species

For charged species we introduce the electrochemical potential,

$$\mu_j^E = \mu_j(\{x_i\}, p, T) + \ z_j \Phi$$

which introduces an additional contribution to the diffusion driving force,

$$\boldsymbol{d}_j = \sum_i^N \Gamma_{ji} \nabla x_i + \frac{\nabla p}{n k_B T} \phi_j + \frac{m_k z_k}{k_B T} \ x_k \nabla \Phi$$

# Nernst-Planck Theory

If we assume that $\boldsymbol{\chi}$ and $\boldsymbol{\Gamma}$ are diagonal and $\nabla p = \nabla T = 0$ then we recover Nernst-Planck theory,

$$\overline{\boldsymbol{F}_k} = -D_k \nabla a_k + M_k x_k \boldsymbol{E}$$

where

$$D_k = \rho_k \chi_{kk} \qquad a_k = \Gamma_{kk} x_k \qquad M_k = \frac{D_k m_k z_k}{k_B T}$$

Diffusion Coefficient

Activity

Mobility

Note that the expression for mobility is the Einstein relation.

# Numerics

Characteristic microscopic length scale in an electrolyte is the Debye length,

$$\lambda_D = \sqrt{\frac{\epsilon \, k_B T}{\sum_k \rho w_k m_k z_k^2}}$$

The fluid is quasi-neutral for length scales significantly larger than the Debye length.

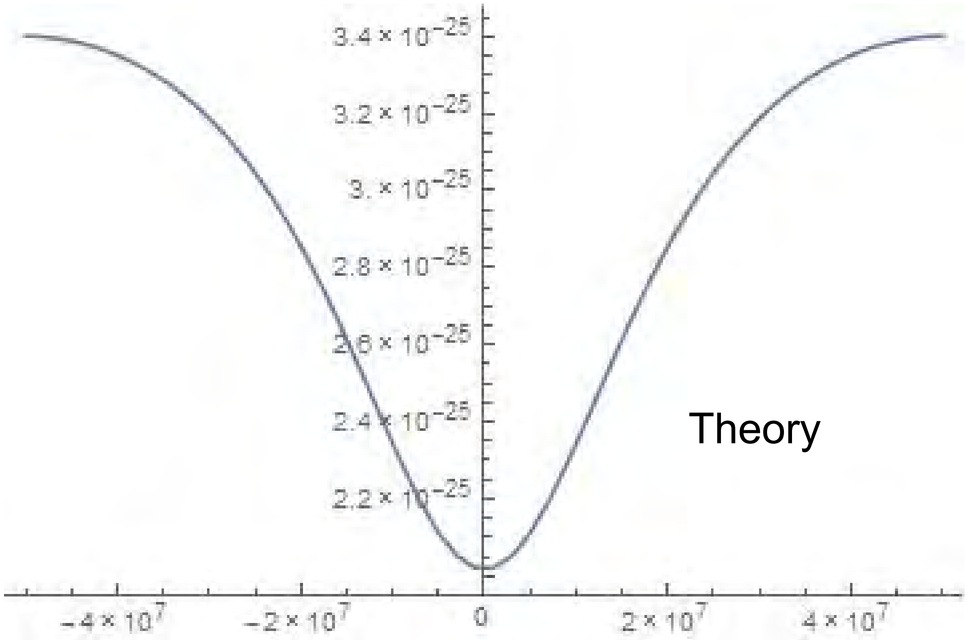
An explicit method may violate quasi-neutrality if the time step is too large, resulting in numerical instability. To remove this stiffness problem an implicit solver is used.

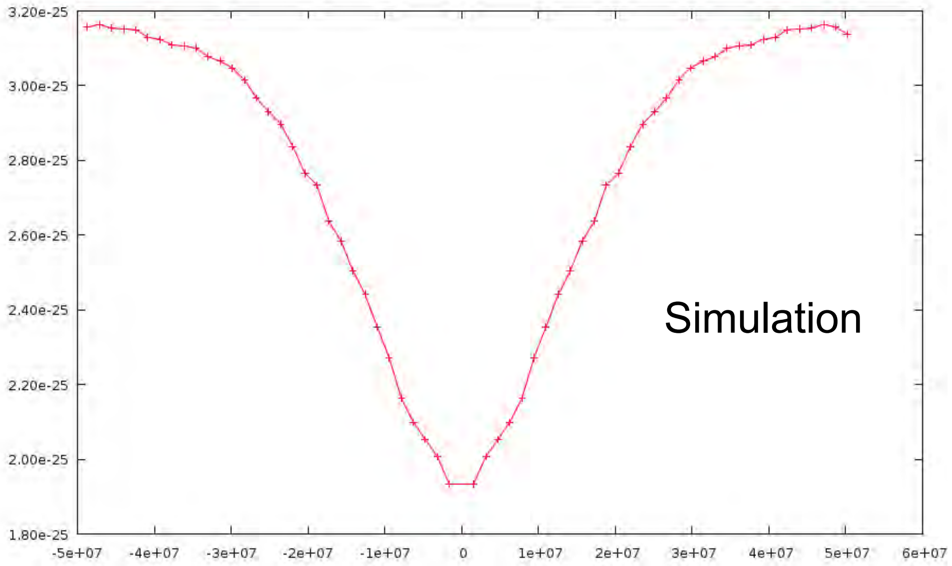
# Structure Factor

Equilibrium structure factor for density fluctuations of sodium ions in sea water.

$$\langle \delta\rho_{\mathrm{Na}}(k)\delta\rho_{\mathrm{Na}}(k)^*\rangle$$

Similar results are found for the chloride ions



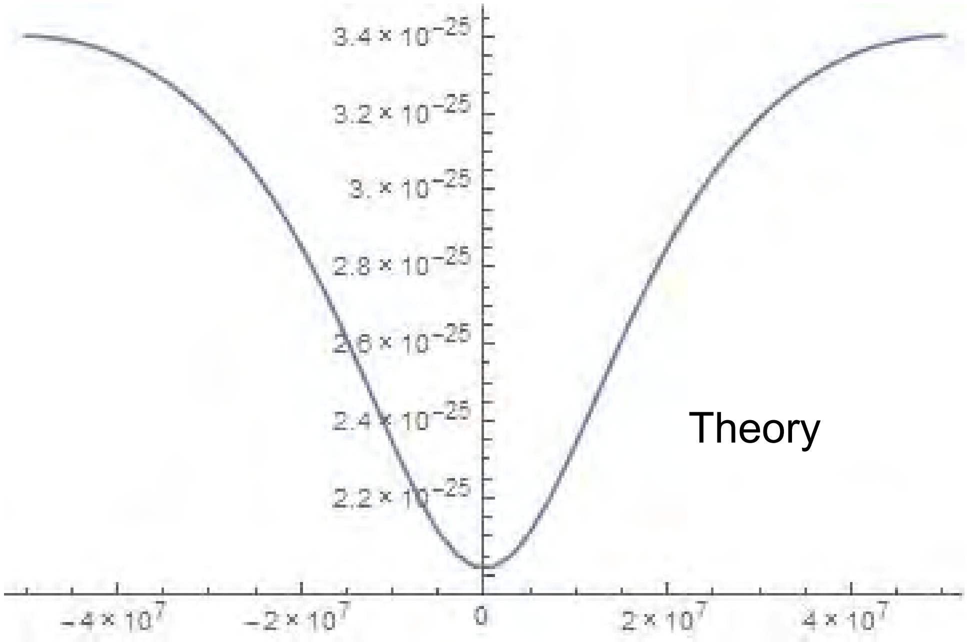


# Structure Factor

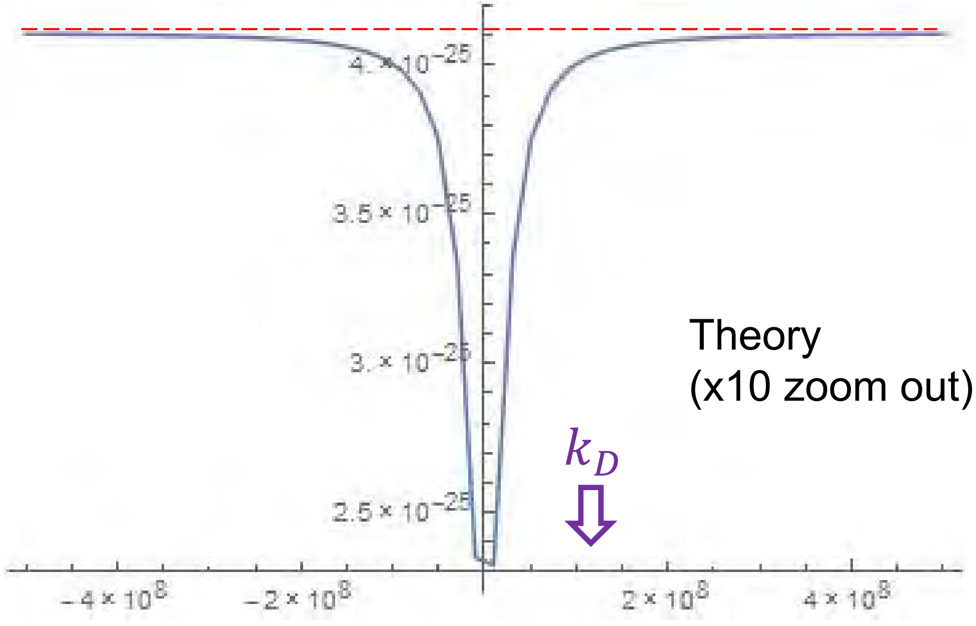
Equilibrium structure factor for density fluctuations of sodium ions in sea water.

$$\langle \delta\rho_{\mathrm{Na}}(k)\delta\rho_{\mathrm{Na}}(k)^{*}\rangle$$

Above the Debye wavenumber, $k_D$, the structure factor goes to the value for neutrals at this density and concentration.



Theory

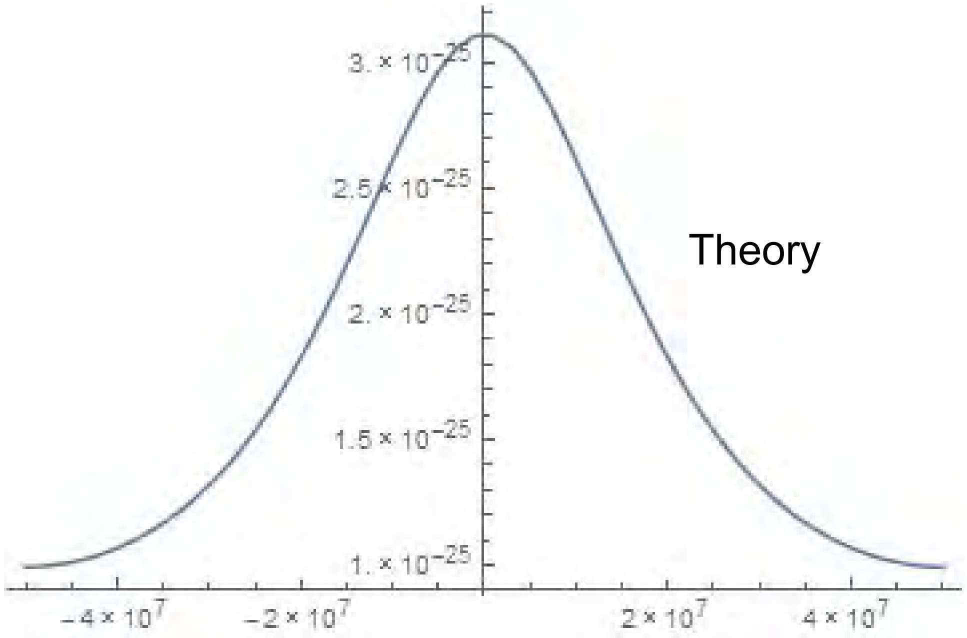


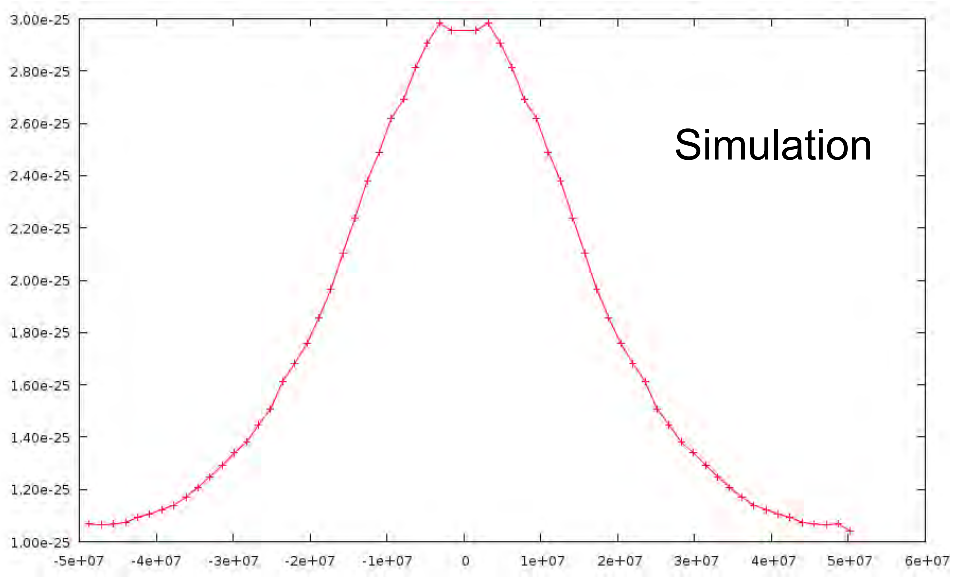
Theory (x10 zoom out)

# Structure Factor

Correlation of density fluctuations of sodium and chloride ions in sea water at equilibrium

$$\langle \delta\rho_{\mathrm{Na}}(k)\,\delta\rho_{\mathrm{Cl}}(k)^{*} \rangle$$



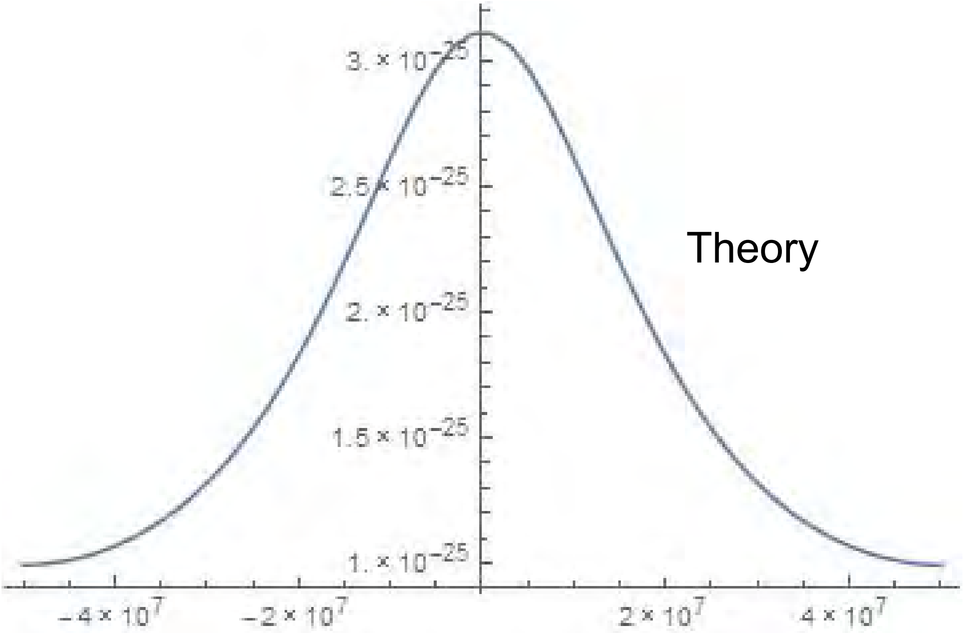


# Structure Factor

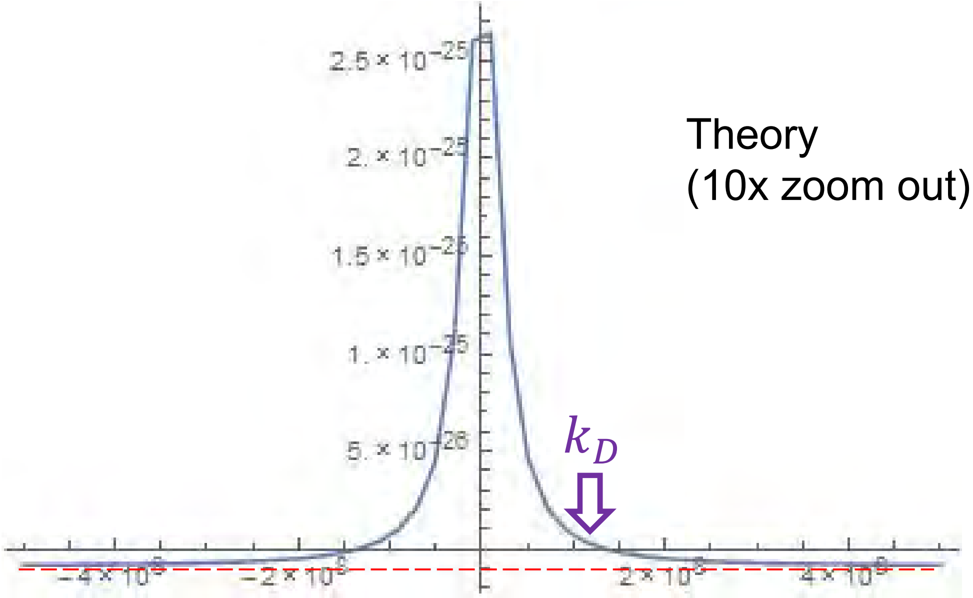
Correlation of density fluctuations of sodium and chloride ions in sea water at equilibrium

$$\langle \delta\rho_{\mathrm{Na}}(k)\delta\rho_{\mathrm{Cl}}(k)^* \rangle$$

Above the Debye wavenumber, $k_D$, the structure factor goes to the value for neutrals (note the small anti-correlation due to the low Mach EOS constraint).



Theory



Theory
(10x zoom out)

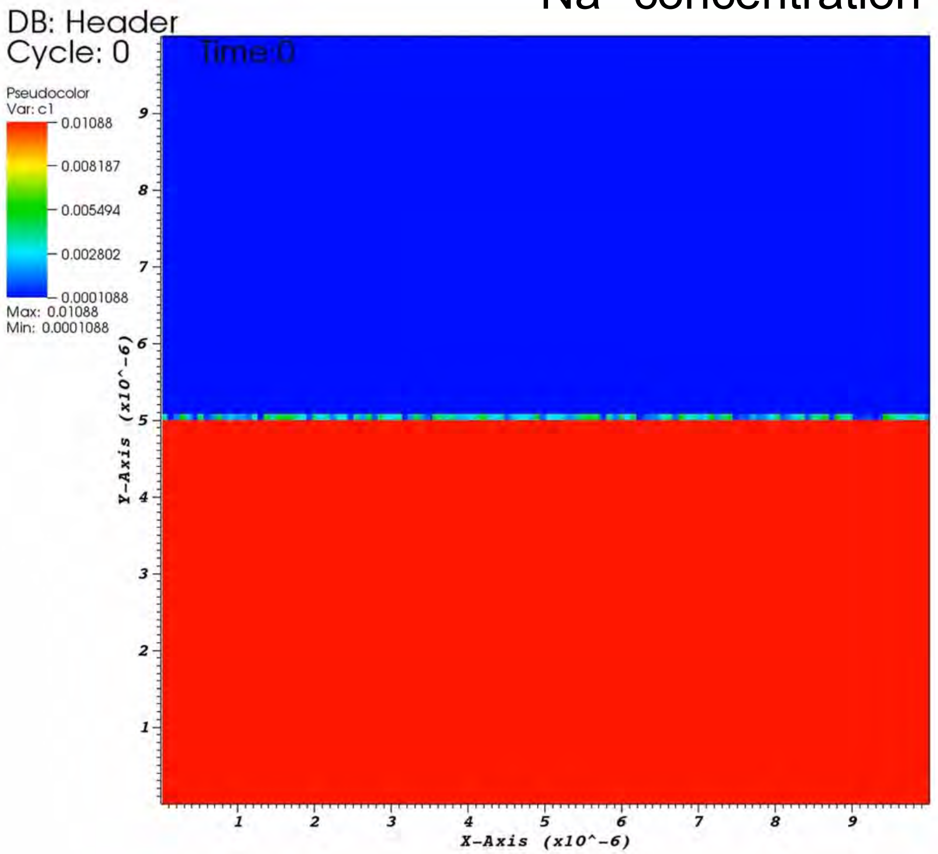
# Free Mixing

Fresh water (top) and sea water (bottom)

Free mixing
(no applied field,
no gravity)

Deterministic simulation with initially perturbed interface

Movie shows
$Na^+$ concentration



$\lambda_D = 0.44$ nm

System width is 0.1 μm

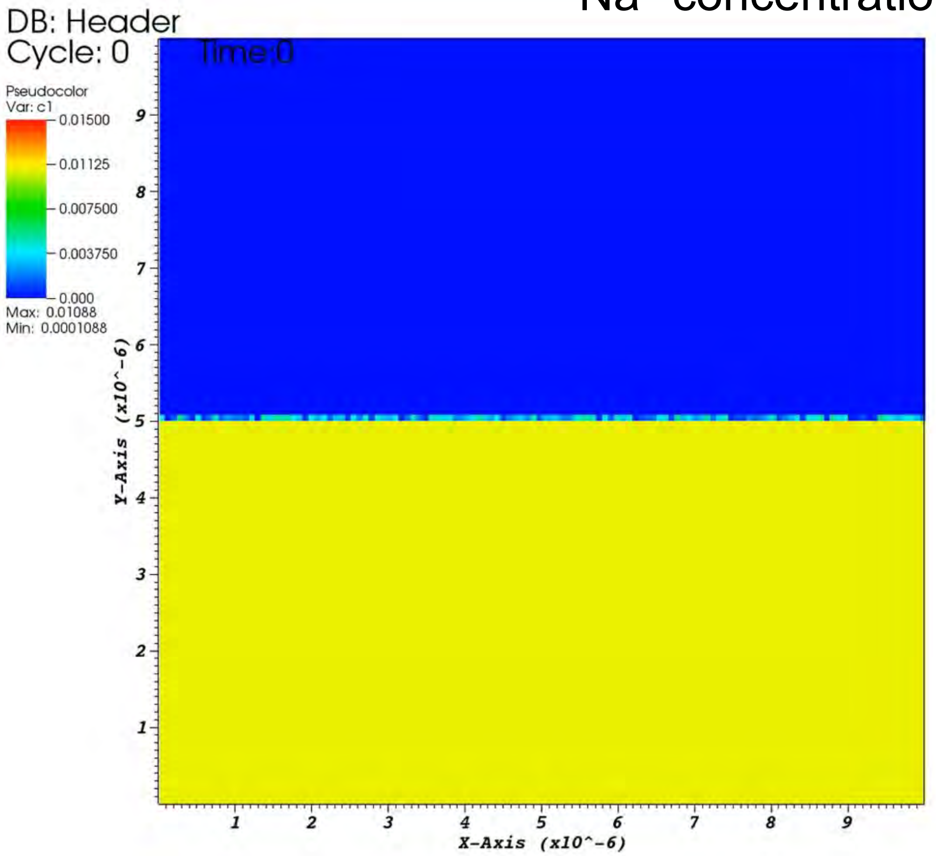
# Free Mixing

Fresh water (top) and sea water (bottom)

Free mixing
(no applied field,
no gravity)

Stochastic
simulation with initially perturbed interface

Movie shows
Na$^+$ concentration



$\lambda_D = 0.44$ nm

System width is 0.1 μm

# Giant Fluctuations

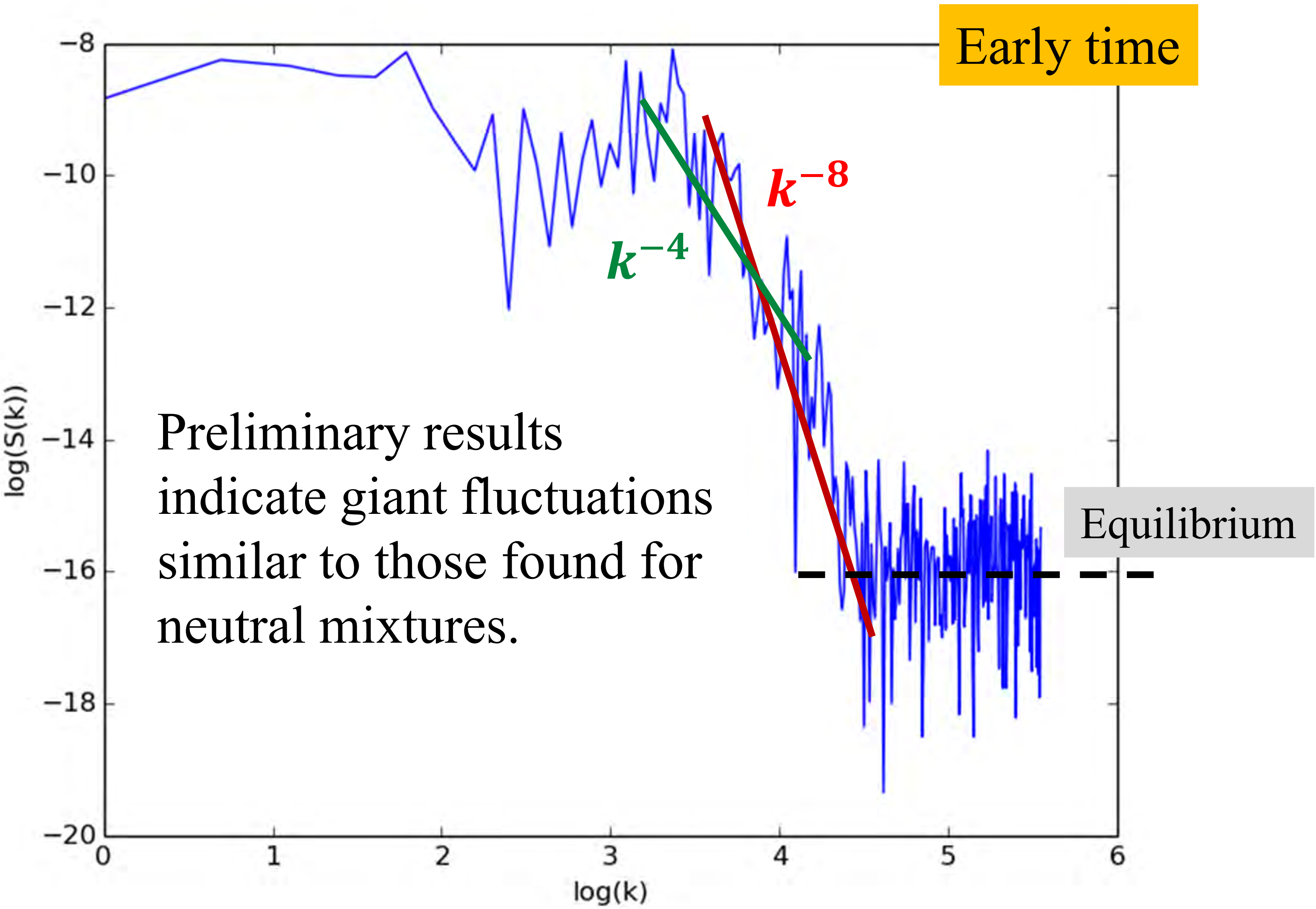
Currently investigating the form of the giant fluctuations in electrolytes.

Movie shows
Na$^+$ concentration

$\lambda_D = 0.44 \text{ nm}$

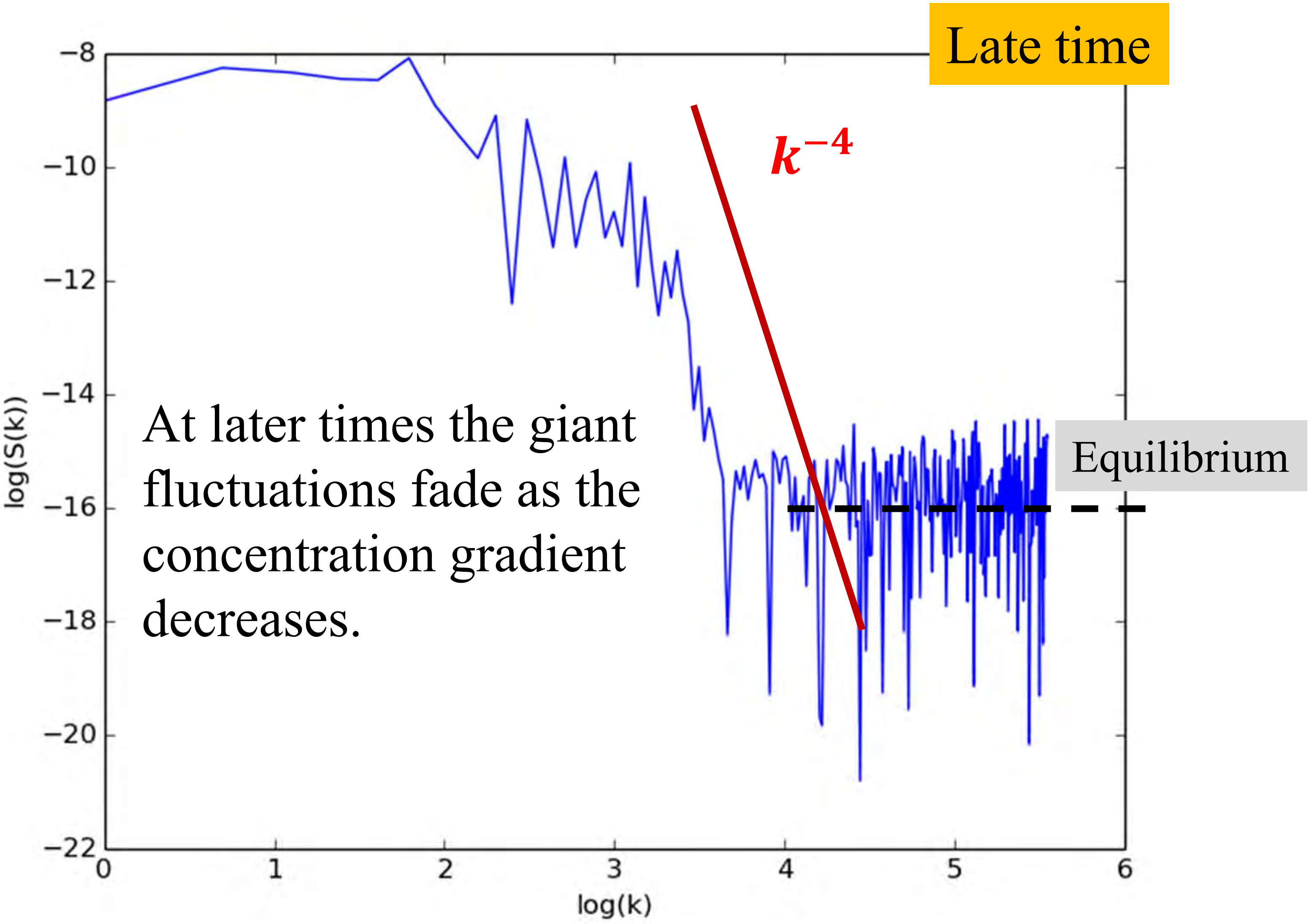
System width is 0.4 μm

# Giant Fluctuations



Preliminary results indicate giant fluctuations similar to those found for neutral mixtures.

# Giant Fluctuations



At later times the giant fluctuations fade as the concentration gradient decreases.

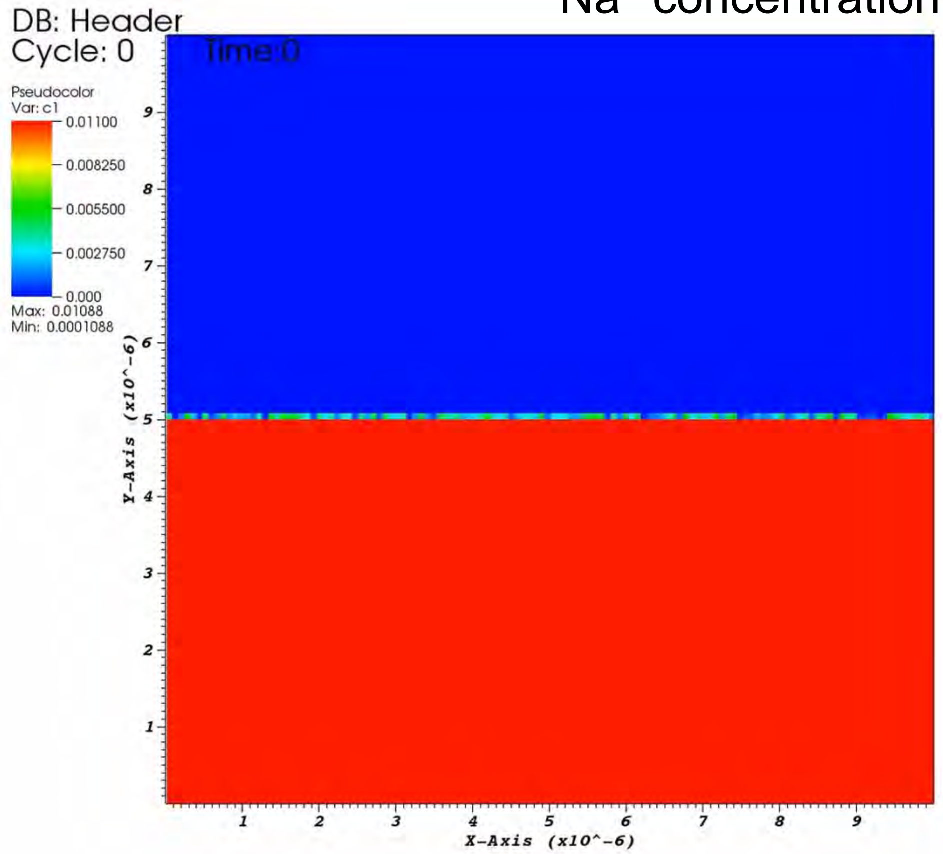
# Forced Mixing

Fresh water (top) and sea water (bottom)

Forced mixing of $10^7$ Volts per meter

Deterministic simulation with initially perturbed interface

Movie shows $Na^+$ concentration



Dielectric strength of water is 7 x$10^7$ V/m

$\lambda_D = 0.44$ nm

System width is 0.1 μm

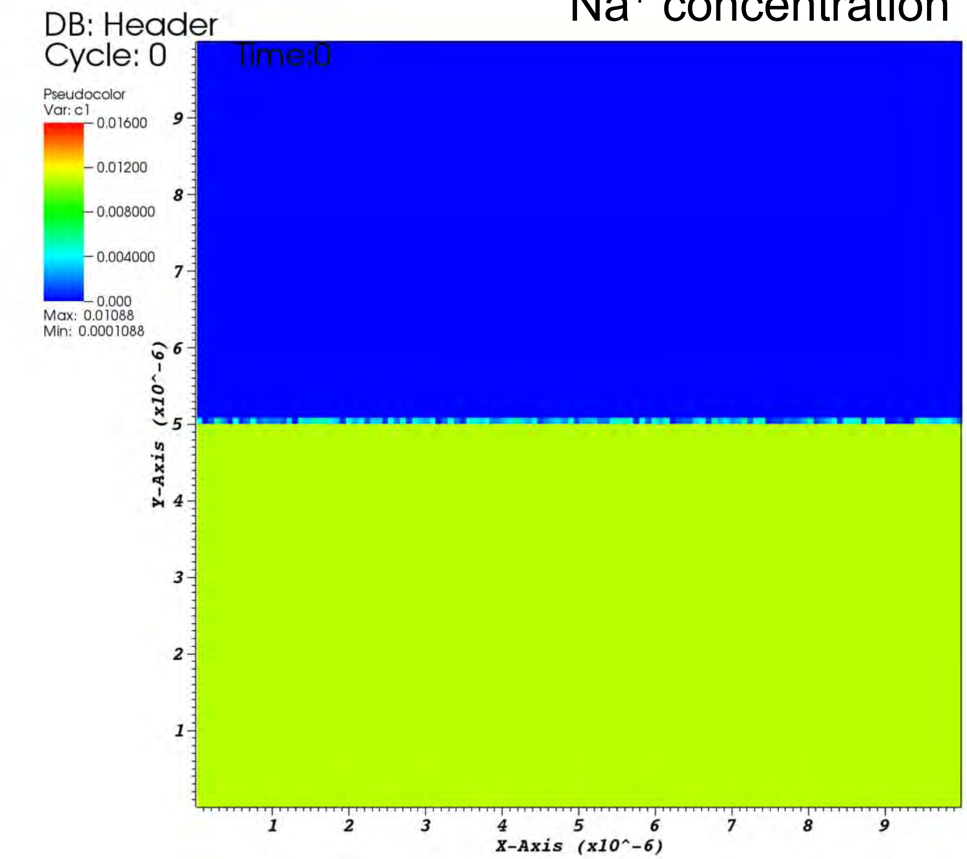
# Forced Mixing

Fresh water (top) and sea water (bottom)

Forced mixing of $10^7$ Volts per meter

Stochastic simulation with initially perturbed interface

Movie shows $Na^+$ concentration



Dielectric strength of water is 7 x$10^7$ V/m

$\lambda_D = 0.44$ nm

System width is 0.1 μm

# Summary & Future Work

Summary:

- Multispecies transport features interesting phenomena.
- Efficient and accurate methods exist for solving fluctuating hydrodynamics of neutral species mixtures.
- The extension to charged species is theoretically straight-forward but presents numerical challenges.

Future work:

- Finish this and publish it
- Polarization effects
- Near-Ambipolar numerical scheme
- Surfaces (e.g., Helmholtz double layer)
- Electro-chemistry