

# *Diffusive Transport Enhanced by Thermal Velocity Fluctuations*

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ICIAM 2011

Vancouver, Canada

July 2011

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# Coarse-Graining for Fluids

- Assume that we have a **fluid** (liquid or gas) composed of a collection of interacting or colliding **point particles**, each having mass  $m_i = m$ , position  $\mathbf{r}_i(t)$ , and velocity  $\mathbf{v}_i$ .
- Because particle interactions/collisions conserve mass, momentum, and energy, the field

$$\tilde{\mathbf{U}}(\mathbf{r}, t) = \begin{bmatrix} \tilde{\rho} \\ \tilde{\mathbf{j}} \\ \tilde{e} \end{bmatrix} = \sum_i \begin{bmatrix} m_i \\ m_i \mathbf{v}_i \\ m_i v_i^2 / 2 \end{bmatrix} \delta[\mathbf{r} - \mathbf{r}_i(t)]$$

captures the slowly-evolving **hydrodynamic modes**, and other modes are assumed to be fast (molecular).

- We want to describe the hydrodynamics at **mesoscopic scales** using a **stochastic continuum approach**.

# Continuum Models of Fluid Dynamics

- Formally, we consider the continuum field of **conserved quantities**

$$\mathbf{U}(\mathbf{r}, t) = \begin{bmatrix} \rho \\ \mathbf{j} \\ e \end{bmatrix} = \begin{bmatrix} \rho \\ \rho \mathbf{v} \\ \rho c_V T + \rho v^2/2 \end{bmatrix} \cong \tilde{\mathbf{U}}(\mathbf{r}, t),$$

where the symbol  $\cong$  means something like approximates over **long length and time scales**.

- Formal coarse-graining of the microscopic dynamics has been performed to derive an **approximate closure** for the macroscopic dynamics.
- This leads to **SPDEs of Langevin type** formed by postulating a random flux term in the usual Navier-Stokes-Fourier equations with magnitude determined from the **fluctuation-dissipation balance** condition, following Landau and Lifshitz.

# The SPDEs of Fluctuating Hydrodynamics

- Due to the **microscopic conservation** of mass, momentum and energy,

$$\partial_t \mathbf{U} = -\nabla \cdot [\mathbf{F}(\mathbf{U}) - \mathcal{Z}] = -\nabla \cdot [\mathbf{F}_H(\mathbf{U}) - \mathbf{F}_D(\nabla \mathbf{U}) - \mathbf{B}\mathcal{W}],$$

where the flux is broken into a **hyperbolic**, **diffusive**, and a **stochastic flux**.

- We assume that  $\mathcal{W}$  can be modeled as spatio-temporal **white noise**, i.e., a Gaussian random field with covariance

$$\langle \mathcal{W}_i(\mathbf{r}, t) \mathcal{W}_j^*(\mathbf{r}', t') \rangle = (\delta_{ij}) \delta(t - t') \delta(\mathbf{r} - \mathbf{r}').$$

- We will consider here binary fluid mixtures,  $\rho = \rho_1 + \rho_2$ , of two fluids that are **indistinguishable**, i.e., have the same material properties.
- We use the **concentration**  $c = \rho_1/\rho$  as an additional primitive variable.

# Compressible Fluctuating Navier-Stokes

Neglecting viscous heating, the equations of **compressible fluctuating hydrodynamics** are

$$\begin{aligned}
 D_t \rho &= -\rho (\nabla \cdot \mathbf{v}) \\
 \rho (D_t \mathbf{v}) &= -\nabla P + \nabla \cdot (\eta \overline{\nabla \mathbf{v}} + \boldsymbol{\Sigma}) \\
 \rho c_v (D_t T) &= -P (\nabla \cdot \mathbf{v}) + \nabla \cdot (\kappa \nabla T + \boldsymbol{\Xi}) \\
 \rho (D_t c) &= \nabla \cdot [\rho \chi (\nabla c) + \boldsymbol{\Psi}],
 \end{aligned}$$

where  $D_t \square = \partial_t \square + \mathbf{v} \cdot \nabla (\square)$  is the advective derivative,

$$\overline{\nabla \mathbf{v}} = (\nabla \mathbf{v} + \nabla \mathbf{v}^T) - 2(\nabla \cdot \mathbf{v}) \mathbf{I}/3,$$

the heat capacity  $c_v = 3k_B/2m$ , and the pressure is  $P = \rho(k_B T/m)$ . The transport coefficients are the **viscosity**  $\eta$ , thermal conductivity  $\kappa$ , and the **mass diffusion coefficient**  $\chi$ .

# Incompressible Fluctuating Navier-Stokes

- Ignoring density and temperature fluctuations, equations of **incompressible isothermal fluctuating hydrodynamics** are

$$\begin{aligned}\partial_t \mathbf{v} &= \mathcal{P} \left[ -\mathbf{v} \cdot \nabla \mathbf{v} + \nu \nabla^2 \mathbf{v} + \rho^{-1} (\nabla \cdot \boldsymbol{\Sigma}) \right] \\ \nabla \cdot \mathbf{v} &= 0 \\ \partial_t c &= -\mathbf{v} \cdot \nabla c + \chi \nabla^2 c + \rho^{-1} (\nabla \cdot \boldsymbol{\Psi}),\end{aligned}$$

where the **kinematic viscosity**  $\nu = \eta/\rho$ , and  $\mathbf{v} \cdot \nabla c = \nabla \cdot (c\mathbf{v})$  and  $\mathbf{v} \cdot \nabla \mathbf{v} = \nabla \cdot (\mathbf{v}\mathbf{v}^T)$  because of incompressibility.

- Here  $\mathcal{P}$  is the orthogonal projection onto the space of divergence-free velocity fields.

# Stochastic Forcing

- The capital Greek letters denote stochastic fluxes that are modeled as **white-noise** random Gaussian tensor and vector fields, with amplitudes determined from the **fluctuation-dissipation balance principle**, notably,

$$\begin{aligned}\Sigma &= \sqrt{2\eta k_B T} \mathcal{W}^{(v)} \\ \Psi &= \sqrt{2m\chi\rho c(1-c)} \mathcal{W}^{(c)},\end{aligned}$$

where the  $\mathcal{W}$ 's denote white random tensor/vector fields.

- Adding stochastic fluxes to the **non-linear** NS equations produces **ill-behaved stochastic PDEs** (solution is too irregular).
- For now, we will simply **linearize** the equations around a **steady mean state**, to obtain equations for the fluctuations around the mean,

$$\mathbf{U} = \langle \mathbf{U} \rangle + \delta \mathbf{U} = \mathbf{U}_0 + \delta \mathbf{U}.$$



# Nonequilibrium Fluctuations

- When macroscopic gradients are present, steady-state thermal fluctuations become **long-range correlated**.
- Consider a **binary mixture** of fluids and consider **concentration fluctuations** around a steady state  $c_0(\mathbf{r})$ :

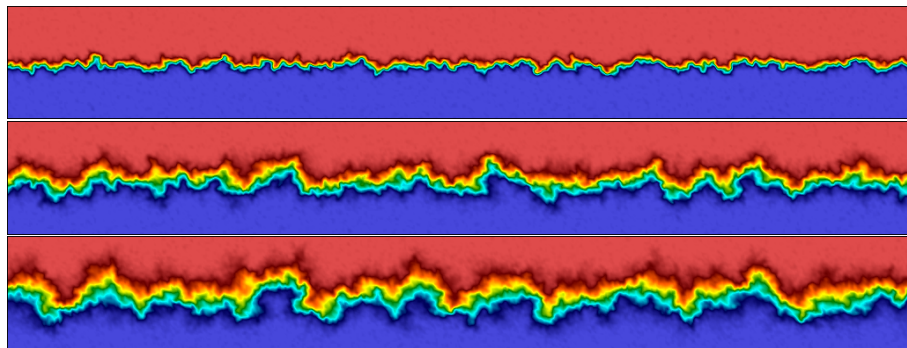
$$c(\mathbf{r}, t) = c_0(\mathbf{r}) + \delta c(\mathbf{r}, t)$$

- The concentration fluctuations are **advected by the random velocities**  $\mathbf{v}(\mathbf{r}, t) = \delta \mathbf{v}(\mathbf{r}, t)$ , approximately:

$$\partial_t (\delta c) + (\delta \mathbf{v}) \cdot \nabla c_0 = \chi \nabla^2 (\delta c) + \sqrt{2\chi k_B T} (\nabla \cdot \mathcal{W}_c)$$

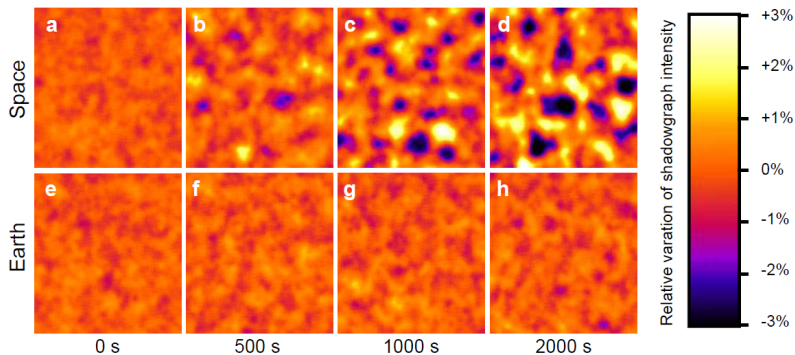
- The velocity fluctuations drive and amplify the concentration fluctuations leading to so-called **giant fluctuations** [1].

# Fractal Fronts in Diffusive Mixing



**Figure:** Snapshots of concentration in a miscible mixture showing the development of a *rough* diffusive interface between two miscible fluids in zero gravity [2, 1, 3].

## Giant Fluctuations in Experiments



**Figure:** Experimental results by A. Vailati *et al.* from a microgravity environment [1] showing the enhancement of concentration fluctuations in space (box scale is **macroscopic**: 5mm on the side, 1mm thick).

# Concentration-Velocity Correlations

- The **nonlinear** concentration equation includes a contribution to the mass flux due to **advection by the fluctuating velocities**,

$$\partial_t (\delta c) + (\delta \mathbf{v}) \cdot \nabla c_0 = \nabla \cdot [ -(\delta c) (\delta \mathbf{v}) + \chi \nabla (\delta c) ] + \dots$$

- The **linearized equations** can be solved in the Fourier domain (ignoring boundaries for now) for any wavenumber  $\mathbf{k}$ , denoting  $k_{\perp} = k \sin \theta$  and  $k_{\parallel} = k \cos \theta$ .
- One finds that **concentration and velocity fluctuations develop long-ranged correlations**:

$$\Delta \mathcal{S}_{c, v_{\parallel}} = \langle (\widehat{\delta c}) (\widehat{\delta v_{\parallel}})^* \rangle = -\frac{k_B T}{\rho(\nu + \chi) k^2} (\sin^2 \theta).$$

- A quasi-linear (perturbative) approximation gives the extra flux [4, 5]:

$$\begin{aligned} \Delta \mathbf{j} &= -\langle (\delta c) (\delta \mathbf{v}) \rangle \approx -\langle (\delta c) (\delta \mathbf{v}) \rangle_{\text{linear}} =, \\ &= - (2\pi)^{-3} \int_{\mathbf{k}} \mathcal{S}_{c, \mathbf{v}} (\mathbf{k}) d\mathbf{k} = (\Delta \chi) \nabla c_0, \end{aligned}$$

# Fluctuation-Enhanced Diffusion Coefficient

- The **fluctuation-renormalized diffusion coefficient** is  $\chi + \Delta\chi$  (think of **eddy diffusivity** in turbulent transport), and we call  $\chi$  the **bare diffusion coefficient** [6].
- The *enhancement*  $\Delta\chi$  due to thermal velocity fluctuations is

$$\Delta\chi = -(2\pi)^{-3} \int_{\mathbf{k}} \Delta\mathcal{S}_{c,v_{\parallel}}(\mathbf{k}) d\mathbf{k} = \frac{k_B T}{(2\pi)^3 \rho (\chi + \nu)} \int_{\mathbf{k}} (\sin^2 \theta) k^{-2} d\mathbf{k}.$$

- Because of the  $k^{-2}$ -like divergence, the integral over all  $\mathbf{k}$  above diverges unless one imposes a lower bound  $k_{min} \sim 2\pi/L$  and a **phenomenological cutoff**  $k_{max} \sim \pi/L_{mol}$  [5] for the upper bound, where  $L_{mol}$  is a “**molecular**” length scale.
- More importantly, the fluctuation enhancement  $\Delta\chi$  **depends on** the small wavenumber cutoff  $k_{min} \sim 2\pi/L$ , where  $L$  is the **system size**.

# System-Size Dependence

- Consider the effective diffusion coefficient in a system of dimensions  $L_x \times L_y \times L_z$  with a concentration gradient imposed along the  $y$  axis.
- In **two dimensions**,  $L_z \ll L_x \ll L_y$ , linearized fluctuating hydrodynamics predicts a **logarithmic divergence**

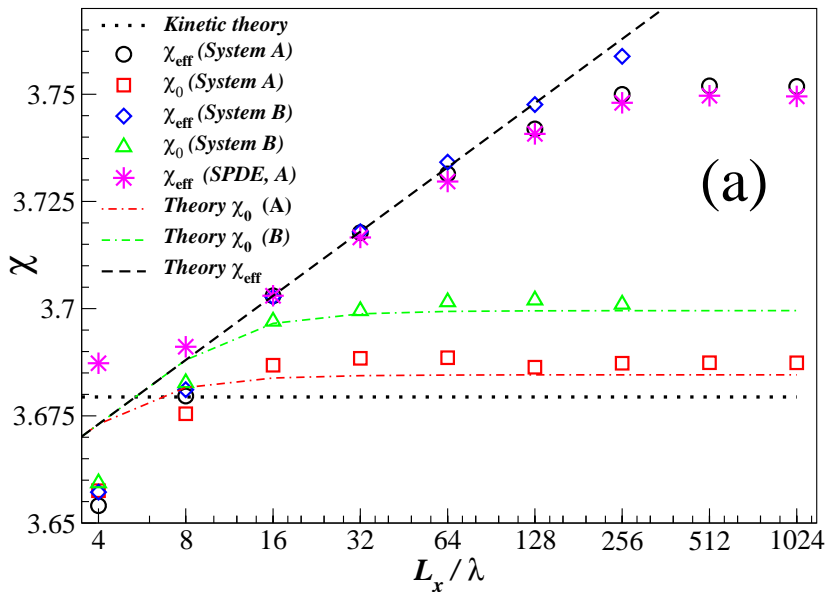
$$\chi_{\text{eff}}^{(2D)} \approx \chi + \frac{k_B T}{4\pi\rho(\chi + \nu)L_z} \ln \frac{L_x}{L_0}$$

- In **three dimensions**,  $L_x = L_z = L \ll L_y$ ,  $\chi_{\text{eff}}$  converges as  $L \rightarrow \infty$  to the **macroscopic diffusion coefficient**,

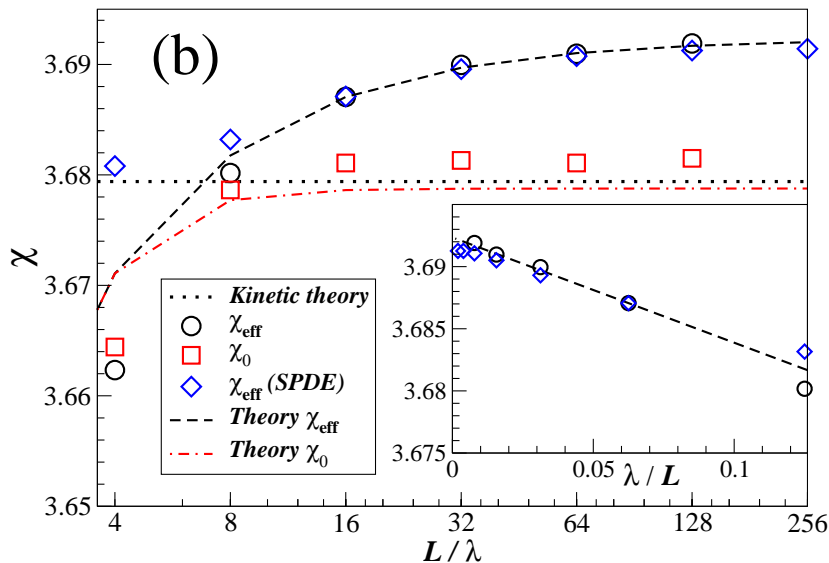
$$\chi_{\text{eff}}^{(3D)} \approx \chi + \frac{\alpha k_B T}{\rho(\chi + \nu)} \left( \frac{1}{L_0} - \frac{1}{L} \right)$$

- We have verified these predictions using particle (DSMC) simulations at hydrodynamic scales [2].

## Particle Simulations



## Three Dimensions





# Microscopic, Mesoscopic and Macroscopic Fluid Dynamics

- Instead of an ill-defined “molecular” or “bare” diffusivity, one should define a **locally renormalized diffusion coefficient**  $\chi_0$  that depends on the length-scale of observation.
- This coefficient accounts for the arbitrary division between continuum and particle levels inherent to fluctuating hydrodynamics.
- A deterministic continuum limit does not exist in two dimensions, and is not applicable to small-scale finite systems in three dimensions.
- **Fluctuating hydrodynamics** is applicable at a broad range of scales if the transport coefficient are renormalized based on the cutoff scale for the random forcing terms.

# Relations to VACF

In the literature there is a lot of discussion about the effect of the **long-time hydrodynamic tail** on the transport coefficients [7],

$$C(t) = \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle \approx \frac{k_B T}{12\rho [\pi(D + \nu)t]^{3/2}} \text{ for } \frac{L_{mol}^2}{(\chi + \nu)} \ll t \ll \frac{L^2}{(\chi + \nu)}$$

*This is in fact **the same effect** as the one we studied!* Ignoring prefactors,

$$\Delta\chi_{VACF} \sim \int_{t=L_{mol}^2/(\chi+\nu)}^{t=L^2/(\chi+\nu)} \frac{k_B T}{\rho[(\chi + \nu)t]^{3/2}} dt \sim \frac{k_B T}{\rho(\chi + \nu)} \left( \frac{1}{L_{mol}} - \frac{1}{L} \right),$$

which is like what we found (all the prefactors are in fact identical also).

# Future Directions

- **Stochastic homogenization:** *Can we write a nonlinear equation that is well-behaved and correctly captures the flow at scales above some chosen “coarse-graining” scale?*
- Other types of nonlinearities in the LLNS equations:
  - Dependence of transport coefficients on fluctuations.
  - Dependence of noise amplitude on fluctuations.
- Transport of other quantities, like momentum and heat.
- Implications to **finite-volume solvers** for fluctuating hydrodynamics.

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