Diffusive Transport Enhanced by Thermal Velocity Fluctuations

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Outline

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

$$\widetilde{\mathbf{U}}(\mathbf{r}, t) = \begin{bmatrix} \tilde{\rho} \\ \tilde{\mathbf{j}} \\ \tilde{e} \end{bmatrix} = \sum_i \begin{bmatrix} m_i \\ m_i \boldsymbol{\upsilon}_i \\ m_i \upsilon_i^2/2 \end{bmatrix} \delta\left[\mathbf{r} - \mathbf{r}_i(t)\right]$$

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**

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

  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,

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

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

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

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

- 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

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

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

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

the heat capacity $c_v=3k_B/2m$, and the pressure is $P=\rho\left(k_BT/m\right)$.
The transport coefficients are the **viscosity** η, thermal conductivity κ, and the **mass diffusion coefficient** χ.

Incompressible Fluctuating Navier-Stokes

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

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

  where the **kinematic viscosity** $\nu = \eta/\rho$, and $\mathbf{v}\cdot\boldsymbol{\nabla}c = \boldsymbol{\nabla}\cdot(c\mathbf{v})$ and $\mathbf{v}\cdot\boldsymbol{\nabla}\mathbf{v} = \boldsymbol{\nabla}\cdot\left(\mathbf{v}\mathbf{v}^T\right)$ 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,

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

  where the $\boldsymbol{\mathcal{W}}$'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:

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

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

Fractal Fronts in Diffusive Mixing

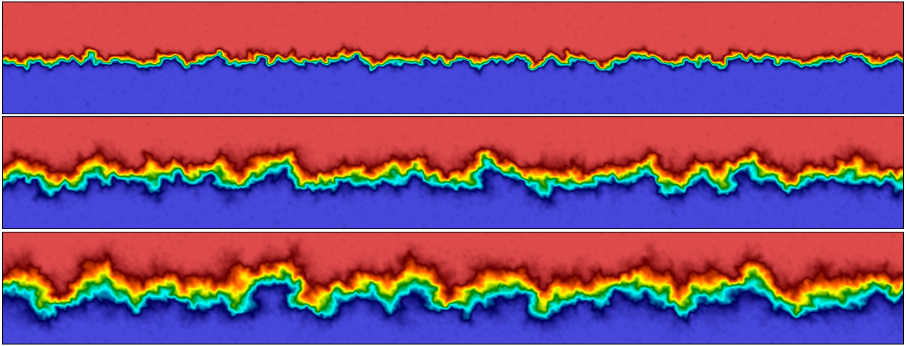


Figure: Snapshots of concentration in a miscible mixture showing the development of a *rough* diffusive interface between two miscible fluids in zero gravity [2, 6, 1, 3].

Giant Fluctuations in Experiments

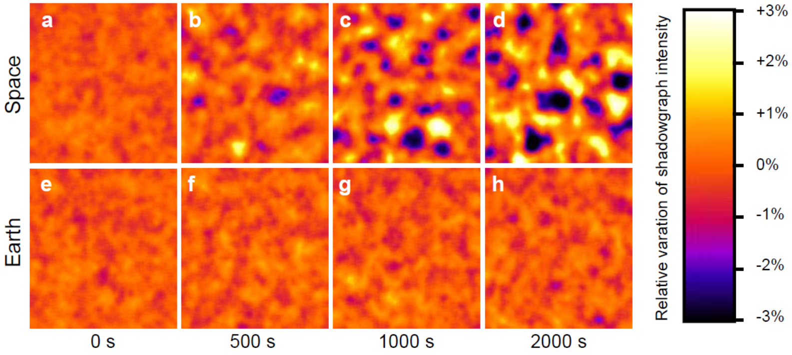


Figure: Experimental results by A. Vailati *et al.* from a microgravity environment [1] showing the enhancement of concentration fluctuations in space (box scale is **macroscopic**: 5mm on the side, 1mm thick).

Concentration-Velocity Correlations

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

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

- 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**:

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

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

$$\Delta \mathbf{j} = -\langle (\delta c)(\delta \mathbf{v}) \rangle \approx -\langle (\delta c)(\delta \mathbf{v}) \rangle_{\text{linear}} =,$$

$$= -(2\pi)^{-3} \int_{\mathbf{k}} \mathcal{S}_{c,\mathbf{v}}(\mathbf{k})\, d\mathbf{k} = (\Delta\chi) \boldsymbol{\nabla} c_0,$$

Fluctuation-Enhanced Diffusion Coefficient

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

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

- 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**

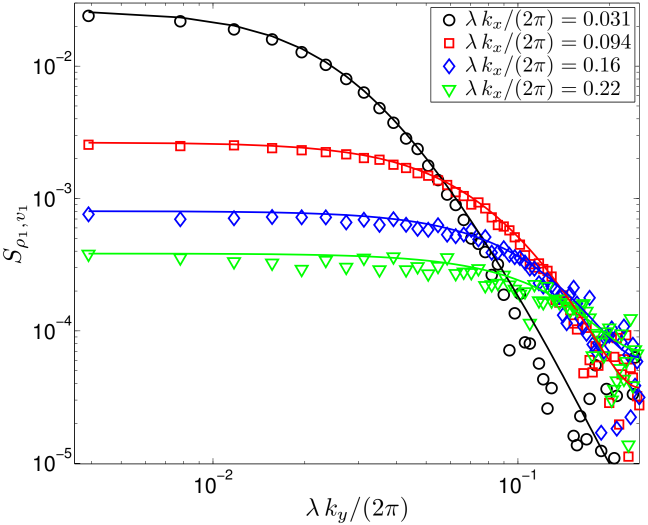
$$\chi_{\text{eff}}^{(2D)} \approx \chi + \frac{k_B T}{4\pi\rho(\chi+\nu)L_z} \ln \frac{L_x}{L_0}$$

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

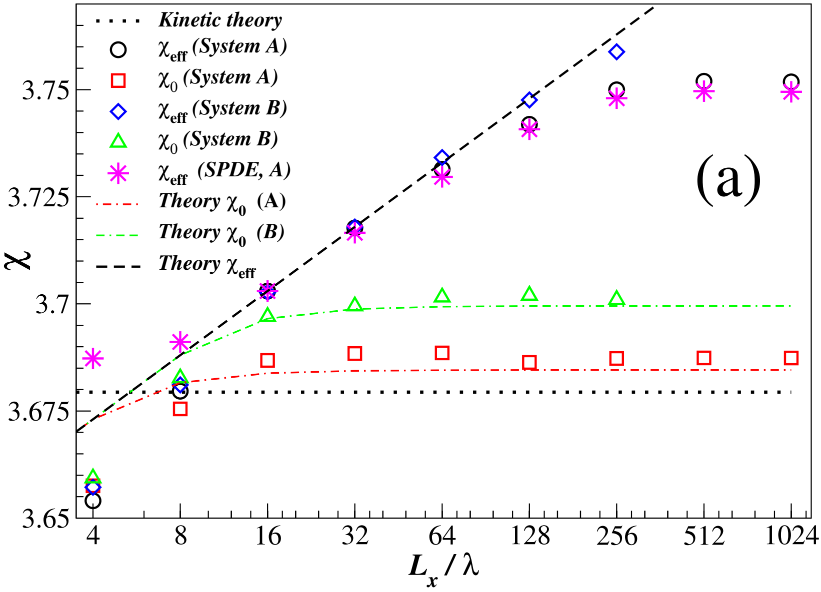
$$\chi_{\text{eff}}^{(3D)} \approx \chi + \frac{\alpha\, k_B T}{\rho(\chi+\nu)} \left(\frac{1}{L_0} - \frac{1}{L} \right)$$

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

Spectra from Particle Simulations



Two Dimensions



Three Dimensions

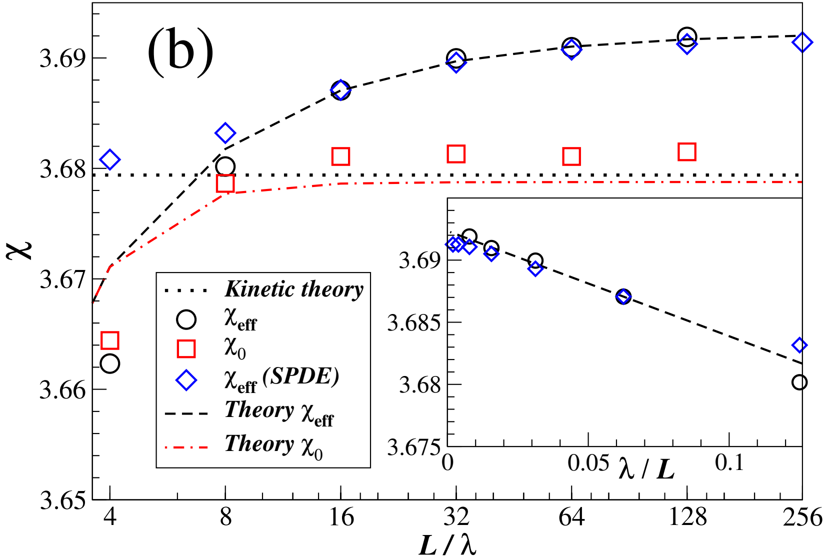


Figure:

Microscopic, Mesoscopic and Macroscopic Fluid Dynamics

- Instead of an ill-defined "molecular" or "bare" diffusivity, one should define a **locally renormalized diffusion coefficient** χ_0 that depends on the length-scale of observation L_{meso}, mesoscopic volume $\Delta\mathcal{V} \sim L_{\text{meso}}^d$.
- This coefficient accounts for the arbitrary division between continuum and particle levels inherent to fluctuating hydrodynamics and eliminates the divergence in the quasi-linearized setting.
- The actual (effective) diffusion coefficient χ_{eff} includes contributions from from all wavenumbers present in the system, while χ_0 only includes "sub-grid" contributions.

$$\chi_{\text{eff}} = \chi_0 \left(\Delta\mathcal{V}\right) - (2\pi)^{-3} \int_{\mathbf{k}} F_{\Delta\mathcal{V}}\left(\mathbf{k}\right) \left[\Delta\mathcal{S}_{c,v_{||}}\left(\mathbf{k}\right)\right] d\mathbf{k},$$

since $F_{\Delta\mathcal{V}}\left(\mathbf{k}\right)$ is a low pass filter with cutoff $2\pi/L_{\text{meso}}$.

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],

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

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

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

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

Conclusions and Future Directions

- 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.
- *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 (transport coefficients, multiplicative noise).
- Transport of other quantities, like momentum and heat.
- Implications to **finite-volume solvers** for fluctuating hydrodynamics.

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