Enhancement of Diffusive Mass Transfer by Thermal Fluctuations

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[1]Work in progress!

Materials WG
February 14th, 2011

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**

$$\mathbf{U}(\mathbf{r},t)=\left[\begin{array}{c}\rho\\ \mathbf{j}\\ e\end{array}\right]=\left[\begin{array}{c}\rho\\ \rho\mathbf{v}\\ \rho c_V T+\rho v^2/2\end{array}\right]\cong\widetilde{\mathbf{U}}(\mathbf{r},t),$$

  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 [1].
- 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.

Incompressible Fluctuating Navier-Stokes

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

$$\begin{aligned} D_t\rho &= -\rho\left(\boldsymbol{\nabla}\cdot\mathbf{v}\right) \\ \rho\left(D_t\mathbf{v}\right) &= -\boldsymbol{\nabla}P + \boldsymbol{\nabla}\cdot\left(\eta\overline{\boldsymbol{\nabla}}\mathbf{v} + \boldsymbol{\Sigma}\right) \\ \rho c_v\left(D_t T\right) &= -P\left(\boldsymbol{\nabla}\cdot\mathbf{v}\right) + \boldsymbol{\nabla}\cdot\left(\kappa\boldsymbol{\nabla}T + \boldsymbol{\Xi}\right) \\ \rho\left(D_t c\right) &= \boldsymbol{\nabla}\cdot\left[\rho\chi\left(\boldsymbol{\nabla}c\right) + \boldsymbol{\Psi}\right], \end{aligned} \tag{1}$$

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 $P = \rho\left(k_B T/m\right)$.
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

$$\begin{aligned} \partial_t \mathbf{v} =& \mathcal{P}\left[-\mathbf{v}\cdot\boldsymbol{\nabla}\mathbf{v} + \nu\boldsymbol{\nabla}^2\mathbf{v} + \rho^{-1}\left(\boldsymbol{\nabla}\cdot\boldsymbol{\Sigma}\right)\right] \quad (2)\\ \boldsymbol{\nabla}\cdot\mathbf{v} =& 0\\ \partial_t c =& -\mathbf{v}\cdot\boldsymbol{\nabla}c + \chi\boldsymbol{\nabla}^2 c + \rho^{-1}\left(\boldsymbol{\nabla}\cdot\boldsymbol{\Psi}\right), \quad (3)\end{aligned}$$

  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,

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

Fluctuations in the presence of gradients

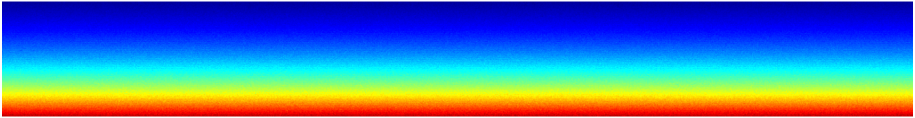
- At **equilibrium**, hydrodynamic fluctuations have non-trivial temporal correlations, but there are no spatial correlations between any variables.
- When macroscopic gradients are present, however, **long-ranged correlated fluctuations** appear.
- Consider a **binary mixture** of fluids and consider **concentration fluctuations** around a non-uniform steady state $c_0(\mathbf{r})$:

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

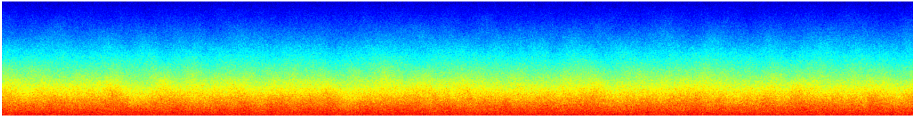
- The velocity fluctuations drive and amplify the concentration fluctuations leading to so-called **giant fluctuations**.

Equilibrium versus Non-Equilibrium

Results obtained using our fluctuating continuum compressible solver.



Concentration for a mixture of two (heavier red and lighter blue) fluids at **equilibrium**, in the presence of gravity.



No gravity but a similar **non-equilibrium** concentration gradient is imposed via the boundary conditions.

Giant Fluctuations during diffusive mixing

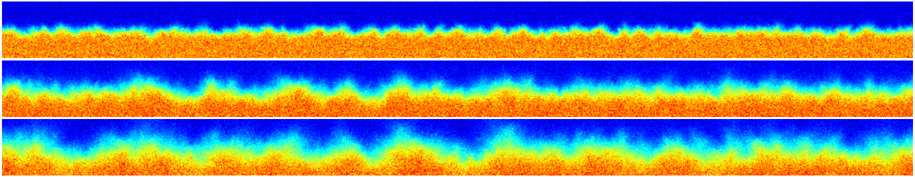


Figure: Snapshots of the concentration during the diffusive mixing of two fluids (red and blue) at $t = 1$ (top), $t = 4$ (middle), and $t = 10$ (bottom), starting from a flat interface (phase-separated system) at $t = 0$.

Giant Fluctuations in Experiments

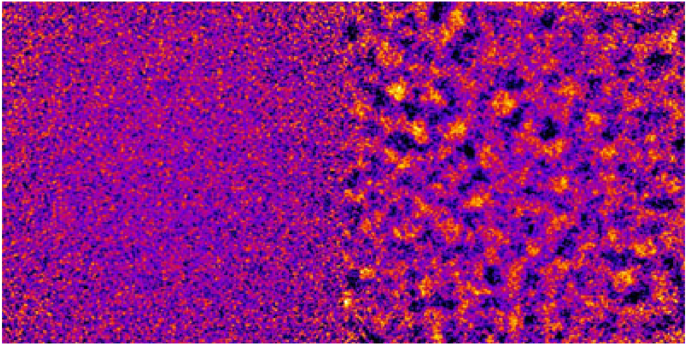


Figure: Experimental snapshots of the steady-state concentration fluctuations in a solution of polystyrene in water with a strong concentration gradient imposed via a stabilizing temperature gradient, in Earth gravity (left), and in microgravity (right) [private correspondence with Roberto Cerbino]. The strong enhancement of the fluctuations in microgravity is evident.

Fluctuation-Enhanced Diffusion Coefficient

- Incompressible (isothermal) **linearized** fluctuating hydrodynamics is given by

$$\partial_t (\delta c) + \mathbf{v} \cdot \boldsymbol{\nabla} c_0 = \chi \boldsymbol{\nabla}^2 (\delta c) + \rho^{-1} \boldsymbol{\nabla} \cdot \left[\sqrt{2m\chi\rho \, c_0(1-c_0)} \boldsymbol{\mathcal{W}}_c \right]$$

$$\mathbf{v}_t = \mathcal{P} \left[\nu \boldsymbol{\nabla}^2 \mathbf{v} + \rho^{-1} \boldsymbol{\nabla} \cdot \left(\sqrt{2\eta k_B T} \, \boldsymbol{\mathcal{W}}^{(\mathbf{v})} \right) \right]$$

- The **nonlinear** concentration equation includes a contribution to the mass flux due to **advection by the fluctuating velocities** [2, 3],

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

- **Does the advective mass flux $-\rho (\delta c) \mathbf{v}$ contribute to the mean (overall) mass transport (mixing rate)?**
  Think about eddy diffusivity in turbulent transport.

Model System

We study the following simple **model steady-state system**, mimicking passive scalar transport in a turbulent field:

A mixture of identical but labeled/colored *(as components 1 and 2) fluids is enclosed in a box of lengths* $L_x \times L_y \times L_z$.

Periodic boundary conditions are applied in the x *(horizontal) and* z *(depth) directions, and impermeable constant-temperature walls are placed at the top and bottom boundaries.*

A weak constant concentration gradient $\boldsymbol{\nabla} c_0 = g_c \hat{\mathbf{y}}$ *is imposed along the* y *axes by enforcing constant concentration boundary conditions at the top and bottom walls.*

Linear SPDE Formalism

No matter what equation is solved, the linearized equations are of the form

$$\partial_t \mathcal{U} = \mathcal{L}\mathcal{U} + \mathcal{K}\mathcal{W}, \tag{4}$$

where $\mathcal{L}$ (the *generator*) and $\mathcal{K}$ (the *filter*) are time-independent linear operators,
and $\mathcal{W}$ is spatio-temporal white noise, i.e., a random Gaussian field with zero mean and covariance

$$\left\langle \mathcal{W}(\mathbf{r},t)\mathcal{W}^{\star}(\mathbf{r}',t')\right\rangle = \delta(t-t')\delta(\mathbf{r}-\mathbf{r}'). \tag{5}$$

We now transform to Fourier space, or any suitable orthonormal basis for the generator with the appropriate boundary conditions. We assume here a small gradient g_c and pretend the system is periodic in y.

Fourier Transforms

We can either use a continuous Fourier transform (along y), **wavevector k**:

$$\mathcal{U}(\mathbf{r},t)=\frac{1}{(2\pi)^d}\int_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}\widehat{\mathcal{U}}(\mathbf{k},t) \tag{6}$$

$$\widehat{\mathcal{U}}(\mathbf{k},t)=\int_{\mathbf{r}\in\mathcal{V}}e^{-i\mathbf{k}\cdot\mathbf{r}}\mathcal{U}(\mathbf{r},t)d\mathbf{r}, \tag{7}$$

or a Fourier series (along x and z), $\mathbf{k}=2\pi\boldsymbol{\kappa}/L$, **wavenumber** $\boldsymbol{\kappa}\in\mathbb{Z}^d$:

$$\mathcal{U}(\mathbf{r},t)=\frac{1}{V}\sum_{\mathbf{k}\in\widehat{\mathcal{V}}}e^{i\mathbf{k}\cdot\mathbf{r}}\widehat{\mathcal{U}}(\boldsymbol{\kappa},t) \tag{8}$$

$$\widehat{\mathcal{U}}(\boldsymbol{\kappa},t)=\int_{\mathbf{r}\in\mathcal{V}}e^{-i\mathbf{k}\cdot\mathbf{r}}\mathcal{U}(\mathbf{r},t)d\mathbf{r}, \tag{9}$$

Solution in Fourier Space

For simplicity I will use the continuous notation but the transformation is simple:

$$\int_k f(k)\, dk \longleftrightarrow \frac{2\pi}{L} \sum_{\kappa} f(\kappa)$$

In Fourier space we get one SODE per wavenumber **k**.

$$\partial_t \widehat{\mathcal{U}} = \widehat{\mathcal{L}} \widehat{\mathcal{U}} + \widehat{\mathcal{K}} \widehat{\mathcal{W}}. \tag{10}$$

$$\left\langle \widehat{\mathcal{W}}(\mathbf{k}, t) \widehat{\mathcal{W}}^{\star}(\mathbf{k}', t') \right\rangle = (2\pi)^4 \, \delta(\mathbf{k} - \mathbf{k}') \delta(t - t'),$$

Structure Factors

The equilibrium distribution (invariant measure) of this is a Gaussian process fully characterized by the covariance or **dynamic structure factor**

$$\widetilde{\boldsymbol{\mathcal{S}}}(\mathbf{k},\mathbf{k}',t)=\left\langle\widehat{\boldsymbol{\mathcal{U}}}(\mathbf{k},t')\widehat{\boldsymbol{\mathcal{U}}}^{\star}(\mathbf{k}',t'+t)\right\rangle,$$

though here we will only be concerned with the **static structure factor** (spectrum):

$$\widetilde{\boldsymbol{\mathcal{S}}}(\mathbf{k},\mathbf{k}',t=0)=\boldsymbol{\mathcal{S}}(\mathbf{k})\,(2\pi)^3\,\delta(\mathbf{k}-\mathbf{k}').$$

Here $\boldsymbol{\mathcal{S}}(\mathbf{k})$ is a self-adjoint matrix of size N_v^2, where N_v is the number of hydrodynamic variables, and it can be obtained by solving the linear system [4]

$$\widehat{\boldsymbol{\mathcal{L}}}\boldsymbol{\mathcal{S}}+\boldsymbol{\mathcal{S}}\left(\widehat{\boldsymbol{\mathcal{L}}}\right)^{\star}=-\widehat{\boldsymbol{\mathcal{K}}}\left(\widehat{\boldsymbol{\mathcal{K}}}^{\star}\right). \tag{11}$$

Solution with Concentration Gradient

$$\partial_t (\delta c) + \mathbf{v} \cdot \mathbf{g}_c = \chi \boldsymbol{\nabla}^2 (\delta c) + \rho^{-1} \boldsymbol{\nabla} \cdot \left[\sqrt{2m\chi\rho \, c(1-c)} \mathcal{W}_c \right]$$

$$\mathbf{v}_t = \mathcal{P} \left[\nu \boldsymbol{\nabla}^2 \mathbf{v} + \rho^{-1} \boldsymbol{\nabla} \cdot \left(\sqrt{2\eta k_B T} \, \mathcal{W}^{(\mathbf{v})} \right) \right]$$

$$\widehat{\mathcal{P}} = \mathbf{I} - k^{-2} (\mathbf{k}\mathbf{k}^\star)$$

The generator and filter in Fourier space are:

$$\widehat{\mathcal{L}} = - \begin{bmatrix} \nu \left(k^2 \mathbf{I} - \mathbf{k}\mathbf{k}^\star \right) & \mathbf{0} \\ \mathbf{g}_c & \chi k^2 \end{bmatrix}$$

$$\text{and } \widehat{\mathcal{K}} \left(\widehat{\mathcal{K}}^\star \right) = \begin{bmatrix} 2\rho^{-1} \nu k_B T \left(k^2 \mathbf{I} - \mathbf{k}\mathbf{k}^\star \right) & \mathbf{0} \\ \mathbf{0} & 2m\chi\rho^{-1} \, c(1-c) \, k^2 \end{bmatrix}$$

Long-Ranged Correlations

To first order in the gradient g_c, the equilibrium spectrum is:

$$\boldsymbol{\mathcal{S}} = \begin{bmatrix} \rho^{-1} k_B T \, \widehat{\boldsymbol{\mathcal{P}}} & g_c \Delta \boldsymbol{\mathcal{S}}^{\star}_{c,\mathbf{v}} \\ g_c \Delta \boldsymbol{\mathcal{S}}_{c,\mathbf{v}} & m\rho^{-1} \, c(1-c) \end{bmatrix},$$

where

$$\Delta \boldsymbol{\mathcal{S}}_{c,\mathbf{v}} = -\rho^{-1} (\nu + \chi)^{-1} k_B T \, k^{-4} \left[\hat{g}_c k^2 - k_{\parallel} \mathbf{k} \right],$$

In particular, denoting $k_{\perp} = k \sin\theta$ and $k_{\parallel} = k \cos\theta$, the important result is that **concentration and velocity fluctuations develop long-ranged correlations**:

$$\Delta \mathcal{S}_{c,v_{\parallel}} = \langle (\widehat{\delta c})(\widehat{\delta v}^{\star}_{\parallel}) \rangle = -\frac{k_B T}{\rho(\nu + \chi) k^2} \left(\sin^2\theta \right). \tag{12}$$

Fluctuation-Enhanced Diffusion

Assuming the advective mass flux can be approximated from the linearized solution:

$$\begin{aligned}\Delta\mathbf{j} &= -\langle(\delta c)(\delta\mathbf{v})\rangle \approx -\langle(\delta c)(\delta\mathbf{v})\rangle_{lin} =, \\ &= -(2\pi)^{-6}\int_{\mathbf{k}} d\mathbf{k}\int_{\mathbf{k}'} d\mathbf{k}'\, \langle\widehat{\delta c}(\mathbf{k},t)\,\widehat{\delta\mathbf{v}}^{\star}(\mathbf{k}',t)\rangle e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} \\ &= -(2\pi)^{-3}\int_{\mathbf{k}} \mathcal{S}_{c,\mathbf{v}}(\mathbf{k})\, d\mathbf{k} = \Delta\chi\,\mathbf{g}_c,\end{aligned}$$

where the *enhancement* $\Delta\chi$ due to thermal velocity fluctuations is

$$\Delta\chi = -(2\pi)^{-3}\int_{\mathbf{k}} \Delta\mathcal{S}_{c,v_{\parallel}}(\mathbf{k})\, d\mathbf{k} = \frac{k_B T}{(2\pi)^3\rho(\chi+\nu)}\int_{\mathbf{k}} \left(\sin^2\theta\right) k^{-2}\, d\mathbf{k}. \tag{13}$$

System-Size Dependence

- The **fluctuation-renormalized diffusion coefficient** is $\chi + \Delta\chi$, and we call χ the **bare diffusion coefficient**.
- Because of the k^{-2}-like divergence, the integral over all **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**.
- For simplicity, I will use integrals over k_x and k_z, but one must remember that these ought to be replaced by discrete sums (done numerically).

Two Dimensions

- Assuming a quasi two-dimensional system, $L_z \ll L_x \ll L_y$, we obtain $\Delta\chi\left(L_x\right) \approx$

$$\frac{k_B T}{(2\pi)^3 \rho\left(\chi+\nu\right)} \frac{2\pi}{L_z} 2 \int_{k_x=2\pi/L_x}^{\pi/L_{mol}} dk_x \int_{k_y=-\infty}^{\infty} dk_y \, \frac{k_x^2}{\left(k_x^2+k_y^2\right)^2}, \tag{14}$$

$$= \frac{k_B T}{4\pi\rho(\chi+\nu)L_z} \ln \frac{L_x}{2L_{mol}} \tag{15}$$

- Notice that L_{mol} is **arbitrary**, since ultimately all we can do is compare a given width L_x to some reference system L_0:

$$\chi_{eff}^{(2D)} \approx \chi + \frac{k_B T}{4\pi\rho(\chi+\nu)L_z} \ln \frac{L_x}{L_0}. \tag{16}$$

- When the system width becomes comparable to the height, **boundaries will intervene** and for $L_x \gg L_y$ the effective diffusion coefficient must become a constant.

Three Dimensions

For a three dimensional system with fixed height, $L_x = L_x = L \ll L_y$, we get $\Delta\chi(L) \approx$

$$\frac{k_B T}{(2\pi)^3 \rho\left(\chi+\nu\right)} 4 \int\int_{(k_x,k_z)\geq 2\pi/L}^{(k_x,k_z)\leq \pi/L_{mol}} dk_z dk_x \int_{k_y=-\infty}^{\infty} dk_y \frac{k_x^2+k_z^2}{\left(k_x^2+k_y^2+k_z^2\right)^2}.$$

$$= \frac{\ln\left(1+\sqrt{2}\right) k_B T}{2\pi\rho(\chi+\nu)}\left(\frac{1}{L_{mol}}-\frac{2}{L}\right)$$

Unlike in two dimensions, the renormalized diffusion coefficient converges as $L \to \infty$ as L^{-1}:

$$\chi_{eff}^{(3D)} \approx \chi + \frac{\ln\left(1+\sqrt{2}\right) k_B T}{\pi\rho(\chi+\nu)}\left(\frac{1}{L_0}-\frac{1}{L}\right). \tag{17}$$

Particle Simulations

- In particle simulations, a uniform concentration gradient along the vertical (y) direction is implemented by randomly changing the label of particles that collide with the top and bottom walls.
- Red particles start moving upward, on average, while blue particles move downward. *If color blind there is no movement*!
- The mass flux can be measured by counting the number of color flips at the top/bottom wall over a long time.
- An alternative is to calculate the average momentum of *all* particles belonging to the first component,

$$\langle \mathbf{J} \rangle = \lim_{T \to \infty} T^{-1} \int_{t=0}^{T} \left[\sum_{1} m_i \mathbf{v}_i(t) \right] dt,$$

  where we evaluate the integral via Monte Carlo **sampling at random times** (snapshots).
- At steady state the two are exactly **equivalent** by Galilean invariance.

Sampling Cells

- To look at spatial dependence of hydrodynamic variables, we must put a **grid of sampling or (hydrodynamic) cells**.
- In each sampling cell we measure the instantaneous values of the **conserved mass**

$$M_1 = \rho_1 \Delta V = c\left(M_1 + M_2\right)$$

and the **momentum** of species 1,

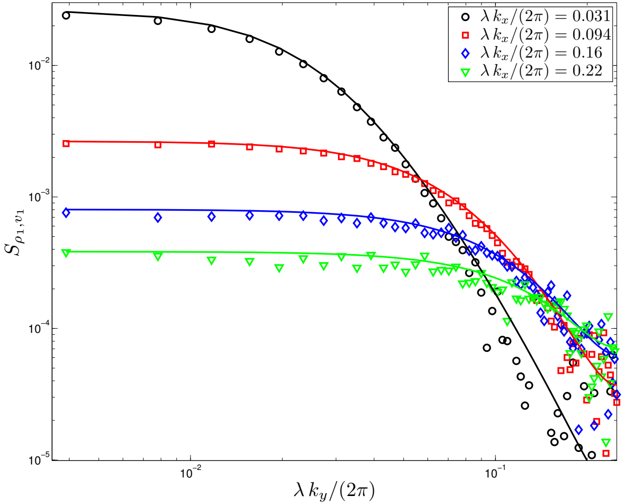
$$j_y = \rho_1 v_{1,y},$$

where $v_{1,y}$ is the **instantaneous velocity** of particles of species 1, and c is the **instantaneous concentration**.
- We also define an average (macroscopic) concentration

$$\bar{c} = \frac{\langle \rho \rangle}{\langle \rho + \rho \rangle} = \frac{\langle \rho_1 \rangle}{\langle \rho_1 + \rho_2 \rangle} \neq \langle c \rangle = \left\langle \frac{\rho_1}{\rho_1 + \rho_2} \right\rangle,$$

since $\langle c \rangle$ is a potentially **biased estimator** of the average concentration.

Spectra from Particle Data



Effective Diffusion

- Because particle collisions preserve color and the only sinks are at the top and bottom walls, the average momentum along the concentration gradient,

$$\langle j_y \rangle = \langle \mathbf{J} \rangle = \langle \rho_1 v_{1,y} \rangle = -\langle \rho_2 v_{2,y} \rangle = \langle \rho_1 \rangle \langle v_{1,y} \rangle + \langle (\delta \rho_1)(\delta v_{1,y}) \rangle, \tag{18}$$

  does not depend on the position or shape of the sampling cell.
- We therefore define the **effective or renormalized diffusion coefficient** χ_{eff},

$$\langle j_y \rangle = \langle \rho_1 v_{1,y} \rangle = \rho_0 \chi_{eff} \, g_c,$$

  where the background concentration gradient is defined as

$$g_c = \frac{\bar{c}_T - \bar{c}_B}{L_y - \Delta y}.$$

Bare Diffusion

- The **bare diffusion coefficient** χ_0 is defined via

$$\langle \rho_1 \rangle \langle v_{1,y} \rangle = \rho_0 \chi_0 \left(\boldsymbol{\nabla}_y \bar{c} \right) \tag{19}$$

  and may depend on y and the shape of the sampling cells.
- Note that $\boldsymbol{\nabla}_y \bar{c} \neq g_c$ since $\bar{c}(y)$ is somewhat nonlinear (we fit a polynomial to $\bar{c}(y)$).
- Deterministic hydrodynamics assumes that χ_0 is a materials constant independent of $\boldsymbol{\nabla} \bar{c}$.
- Note that if we had used g_c instead of $d\bar{c}(y)/dy$ we would get a strong dependence $\chi_0(y)$.

Test of Constitutive Model

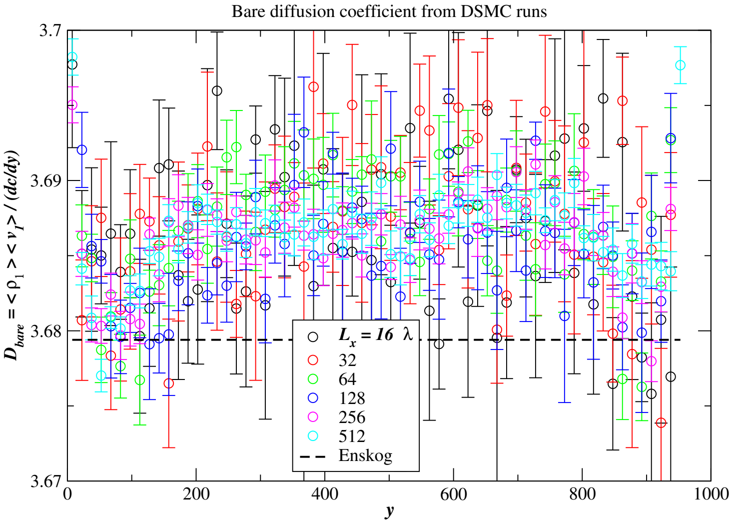


Figure: Particle data for $\chi_0(y)$ in 2D.

Two Dimensions

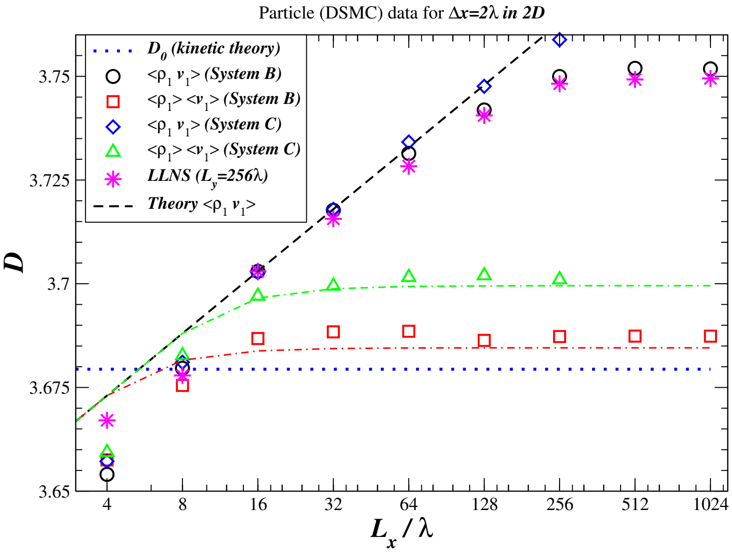


Figure: Diffusion enhancement in two dimensions

Boundary Effects

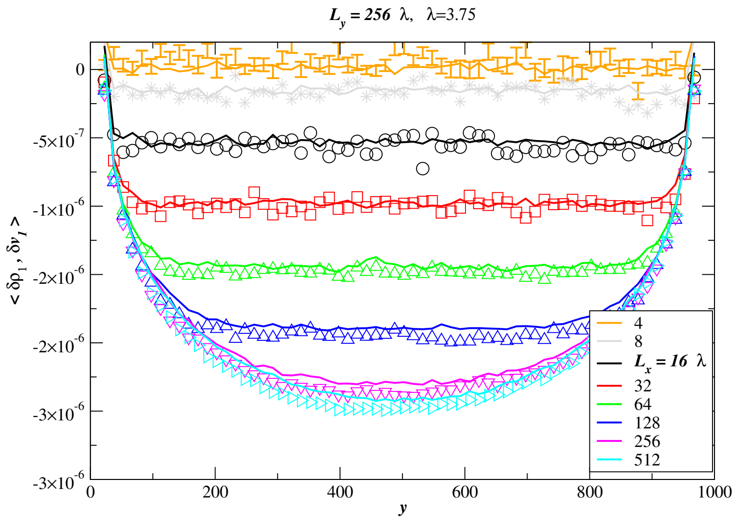


Figure: Spatial dependence of stochastic advective flux.

Three Dimensions

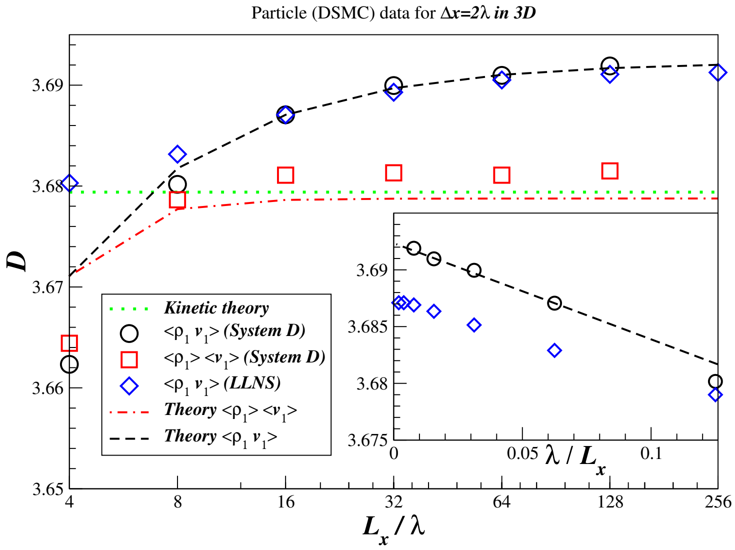


Figure: Diffusion Enhancement in three dimensions.

Theory for bare diffusion χ_0

We have steady-state (ensemble) averages of *finite-volume averages* of the hydrodynamic fields over a hydrodynamic cell $\Delta\mathcal{V}$ of volume $\Delta V = \Delta x \cdot \Delta y \cdot \Delta z$:

$$\rho_0 = \langle \rho \rangle_{\Delta V} = \Delta V^{-1} \langle \int_{\Delta\mathcal{V}} \rho\left(\mathbf{r}, t\right)\, d\mathbf{r} \rangle.$$

Assume that $j = \rho v$, where ρ and v are random Gaussian fields with known correlation

$$\left\langle \widehat{\delta\rho}(\mathbf{k}, t) \widehat{\delta v}^{\star}(\mathbf{k}', t) \right\rangle = \mathcal{S}_{\rho,v}\left(\mathbf{k}\right) \left(2\pi\right)^3 \delta(\mathbf{k} - \mathbf{k}'). \tag{20}$$

The mean instantaneous velocity in a given cell is

$$\langle v \rangle_{\Delta V}^{inst} = \left\langle \frac{\int_{\Delta\mathcal{V}} \rho v \, d\mathbf{r}}{\int_{\Delta\mathcal{V}} \rho \, d\mathbf{r}} \right\rangle \neq \langle v \rangle_{\Delta V} \neq \frac{\langle j \rangle_{\Delta V}}{\langle \rho \rangle_{\Delta V}}.$$

contd.

By expanding to second (quadratic) order in the fluctuations, we obtain

$$\rho_0 \langle v \rangle_{\Delta V}^{inst} = \rho_0 \left\langle \frac{\int_{\Delta\mathcal{V}} (\rho_0 + \delta\rho)(v_0 + \delta v)\ d\mathbf{r}}{\int_{\Delta\mathcal{V}} (\rho_0 + \delta\rho)\ d\mathbf{r}} \right\rangle = \langle \rho v \rangle_{\Delta V} - \Delta j_F, \qquad (21)$$

in which the actual mass flux

$$\langle \rho v \rangle_{\Delta V} = j = \rho_0 v_0 + \langle (\delta\rho)(\delta v) \rangle_{\Delta V} = j_0 + \Delta j,$$

is reduced by

$$\Delta j_F = \Delta V^{-2} \int_{\Delta\mathcal{V}} d\mathbf{r} \int_{\Delta\mathcal{V}} d\mathbf{r}' \ \langle \rho(\mathbf{r}, t) v(\mathbf{r}', t) \rangle$$

Fourier formulation

$$
\begin{aligned}
\Delta j =& \langle (\delta\rho)(\delta v) \rangle_{\Delta V} = \\
=& \Delta V^{-1} \int_{\Delta\mathcal{V}} d\mathbf{r} \; (2\pi)^{-6} \int_{\mathbf{k}} d\mathbf{k} \int_{\mathbf{k}'} d\mathbf{k}' \; \langle \widehat{\delta\rho}(\mathbf{k},t) \, \widehat{\delta v}^{\star}(\mathbf{k}',t) \rangle e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} \\
=& (2\pi)^{-3} \int_{\mathbf{k}} \mathcal{S}_{\rho,v}(\mathbf{k}) \; d\mathbf{k}
\end{aligned}
$$

$$
\begin{aligned}
\Delta j_F =& \Delta V^{-2} \int_{\Delta\mathcal{V}} d\mathbf{r} \int_{\Delta\mathcal{V}} d\mathbf{r}' \; \left\langle \rho(\mathbf{r},t) v(\mathbf{r}',t) \right\rangle = \Delta V^{-2} \int_{\Delta\mathcal{V}} d\mathbf{r} \int_{\Delta\mathcal{V}} d\mathbf{r}' \\
=& (2\pi)^{-6} \int_{\mathbf{k}} d\mathbf{k} \int_{\mathbf{k}'} d\mathbf{k}' \; \langle \widehat{\delta\rho}(\mathbf{k},t) \, \widehat{\delta v}^{\star}(\mathbf{k}',t) \rangle e^{i(\mathbf{k}\cdot\mathbf{r}-\mathbf{k}'\cdot\mathbf{r}')} \\
=& (2\pi)^{-3} \int_{\mathbf{k}} \left[\Delta V^{-2} \int_{\Delta\mathcal{V}} d\mathbf{r} \int_{\Delta\mathcal{V}} d\mathbf{r}' \; e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \right] \mathcal{S}_{\rho,v}(\mathbf{k}) \; d\mathbf{k} \\
=& (2\pi)^{-3} \int_{\mathbf{k}} F(\mathbf{k}) \, \mathcal{S}_{\rho,v}(\mathbf{k}) \; d\mathbf{k}.
\end{aligned}
$$

contd.

$$\rho_0 \chi_{eff} = \chi - (2\pi)^{-3} \int_{\mathbf{k}} \Delta \mathcal{S}_{\rho_1, v_{1,\parallel}} (\mathbf{k}) \; d\mathbf{k}$$

$$\rho_0 \chi_0 = \chi - (2\pi)^{-3} \int_{\mathbf{k}} \left[1 - F(\mathbf{k}) \right] \Delta \mathcal{S}_{\rho_1, v_{1,\parallel}} (\mathbf{k}) \; d\mathbf{k}, \tag{22}$$

Here $F(\mathbf{k})$ is a product of low pass filters, one for each dimension,

$$F_x(k_x) = 2 \left[1 - \cos(k_x \Delta x) \right] / (k_x \Delta x)^2 = \text{sinc}^2(k_x \Delta x / 2).$$

The actual (effective) diffusion coefficient χ_{eff} includes contributions from $\Delta \mathcal{S}_{\rho_1, v_1}$ from all wavenumbers present in the system, while the apparent (bare) χ_0 only includes "sub-grid" contributions, from wavenumbers larger than $2\pi/\Delta x$.

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 [6],

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

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

$$\Delta\chi_{VACF} \sim \int_{t=L_{mol}^2/(\chi+\nu)}^{t=L^2/(\chi+\nu)} \frac{k_B T}{\rho \left[(\chi + \nu) t\right]^{3/2}} dt \sim \frac{k_B T}{\rho (\chi + \nu)} \left(\frac{1}{L_{mol}} - \frac{1}{L} \right), \tag{23}$$

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

Relations to Finite-Size Effects in MD

- In the MD literature, the dependence on L^{-1} in Eq. (23) is considered a finite-size effect that ought to be removed in order to extract the bulk ($L \to \infty$) limit of the diffusion coefficient.
- An Oseen-tensor based theory in Ref. [7] gives exactly the same result for the effective diffusion as fluctuating hydrodynamics.
- The direct connection to the VACF tail, however, does not seem to be appreciated. For example, Ref. [7] claims that "the hydrodynamic correction developed here is not concerned with so-called hydrodynamic long-time tails in, e.g., the particle velocity autocorrelation function."

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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