Computer Simulations of Giant Fluctuations

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IMT12, Madrid, May 2016
Collaborators

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- A number of postdocs and graduate students at Courant and LBL
- A number of experimentalists (Italy, France) present at this meeting.
The thermal velocity fluctuations are described by the (unsteady) fluctuating Stokes equation,

$$\rho \partial_t \mathbf{v} + \nabla \pi = \eta \nabla^2 \mathbf{v} + \sqrt{2 \eta k_B T} \nabla \cdot (\sigma * \mathbf{W}), \quad \text{and} \quad \nabla \cdot \mathbf{v} = 0. \quad (1)$$

where the stochastic momentum flux is spatio-temporal white noise,

$$\langle \mathbf{W}_{ij}(r, t) \mathbf{W}_{kl}^*(r', t') \rangle = (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \delta(t - t') \delta(r - r').$$

and the smoothing kernel $\sigma$ filters out features at scales below a cutoff scale $\sigma$.

The concentration $c(r, t)$ of a passive tracer follows an (additive noise) fluctuating advection-diffusion equation,

$$\partial_t c = -\mathbf{u} \cdot \nabla c + \chi_0 \nabla^2 c. \quad (2)$$
Snapshots of concentration in a miscible mixture showing the development of a *rough* diffusive interface due to the effect of *thermal fluctuations*. These *giant fluctuations* have been studied experimentally and with hard-disk molecular dynamics.
Figure: Discrete spatial spectrum of the interface fluctuations, for fluctuating hydrodynamics (squares) and HD-MD (circles).
In liquids molecules are caged (trapped) for long periods of time as they collide with neighbors:

**Momentum and heat diffuse much faster than does mass.**

This means that \( \chi \ll \nu \), leading to a **Schmidt number**

\[
S_c = \frac{\nu}{\chi} \sim 10^3 - 10^4.
\]

This **extreme stiffness** solving the concentration/tracer equation numerically challenging.

There exists a **limiting (overdamped) dynamics** for \( c \) in the limit \( S_c \to \infty \) in the scaling

\[
\chi \nu = \text{const.}
\]
Adiabatic mode elimination gives the following limiting Ito stochastic advection-diffusion equation,

$$\partial_t c = \nabla \cdot [\chi(r) \nabla c] - \mathbf{w} \cdot \nabla c,$$

which is exactly the same as what was derived from Brownian dynamics.

The advection velocity $\mathbf{w}(r, t)$ is white in time, with covariance proportional to a Green-Kubo integral of the velocity auto-correlation function,

$$\langle \mathbf{w}(r, t) \otimes \mathbf{w}(r', t') \rangle = 2 \delta(t - t') \int_0^\infty \langle \mathbf{u}(r, t) \otimes \mathbf{u}(r', t + t') \rangle dt'$$

$$= 2 \mathbf{R}(r, r') \delta(t - t')$$

$$= \frac{k_B T}{\eta} \int \sigma(r, q') \mathbf{G}(r', r'') \sigma^T(r'', q'') dq' dq''$$,

where $\mathbf{G}$ is the Green’s function for steady Stokes flow with the appropriate boundary conditions.
Experimental results by A. Vailati et al. from a microgravity environment showing **giant fluctuations** in the concentration of polystyrene in toluene in space (box scale is 5mm on the side, 1mm thick).

**Fluctuations become macroscopically large at macroscopic scales!**

These come because of **hydrodynamic effects** on diffusion in liquids.
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 macroscopic state \( \bar{c}(r, t) \), \( c = \bar{c} + \delta c \).

The concentration fluctuations are **advected by the random velocities**,

\[
\partial_t \bar{c} = \chi \nabla^2 \bar{c}
\]

\[
\partial_t \left( \delta c \right) = -\mathbf{v} \cdot \nabla \bar{c} + \chi \nabla^2 \delta c + \nabla \cdot \left( \sqrt{2\chi \bar{c}} \mathbf{W}_c \right)
\]

\[
\rho \partial_t \mathbf{v} + \nabla \pi = \eta \nabla^2 \mathbf{v} - \beta \rho \left( \delta c \right) \mathbf{g} + \sqrt{2\eta k_B T} \nabla \cdot \mathbf{W},
\]

where \( \beta \) is the solutal expansion coefficient. This system of SPDEs can easily be solved numerically once we take the **overdamped limit**.

Note that here \( \chi \) is the deterministic (Fickian) diffusion coefficient which is **larger** than the bare \( \chi_0 \).
The coupled \textit{linearized velocity}-concentration system in \textbf{one dimension}:

\begin{align*}
\nu_t &= \nu \nu_{xx} + \sqrt{2\rho^{-1}} \nu \, W_x \\
c_t &= \chi c_{xx} - \nu \bar{c}_x,
\end{align*}

where \( \bar{c}_x \) is the imposed background concentration gradient.

The linearized system can be easily solved in Fourier space to give a \textbf{power-law divergence} for the spectrum of the concentration fluctuations as a function of wavenumber \( k \),

\begin{align*}
\langle \hat{c} \hat{c}^* \rangle &= \rho \frac{k_B T}{\chi (\chi + \nu) k^4} (\bar{c}_x)^2 \approx \frac{k_B T}{\chi \eta k^4} (\bar{c}_x)^2 \quad \text{for large Sc.}
\end{align*}

Concentration fluctuations become \textbf{long-ranged} and are \textbf{enhanced} as the square of the gradient, to values much larger than equilibrium fluctuations.

In real life the divergence is \textbf{suppressed} by \textbf{surface tension, gravity, or boundaries} (usually in that order).
Simulation versus Theory/Experiment

1. Simulations have the following advantages over analytical theory:
   - Numerical linearization around arbitrary time-dependent macroscopic states including nonlinearities (e.g., chemistry).
   - Nontrivial boundary conditions can be accounted for relatively easily.

2. Simulations have the following advantages over experiments:
   - One can easily turn different effects/terms on and off to understand what physics is important.
   - No measurement noise or contamination, but still includes thermal fluctuations.

3. Disadvantages of simulations include:
   - Fluctuations imply statistical noise, so long runs needed to compute averages (Monte Carlo).
   - Cannot easily handle time and length scale separation.
   - Development of computer codes is like developing a new experimental apparatus; it takes time!
We numerically solve the equations

\[ \rho \partial_t v + \nabla \pi = \eta \nabla^2 v + \nabla \cdot \left( \sqrt{2\eta k_B T_0} \mathcal{W} \right) \]  
\[ \nabla \cdot v = 0 \]  
\[ \partial_t c + v \cdot \nabla c = D \nabla \cdot (\nabla c + c(1-c) S_T \nabla T) \]  
\[ \partial_t T + v \cdot \nabla T = \kappa \nabla^2 T, \]

Our numerical methods perform numerical linearization by solving the fully nonlinear equations with weak noise.

In the linearized regime no difference between 2D and 3D so we sometimes solve 2D equations to speed up computations.

Numerically we separately solve (4,5) for concentration (overdamped), and we separately solve (4,6) for temperature (inertial) [1].
The limiting dynamics can be efficiently simulated using the following **predictor-corrector algorithm** (implemented on GPUs):

1. Generate a random advection velocity by solving **steady Stokes** with random forcing,

\[
\nabla \pi^{n+\frac{1}{2}} = \nu \left( \nabla^2 v^n \right) + \Delta t^{-\frac{1}{2}} \nabla \cdot \left( \sqrt{2\nu \rho^{-1} k_B T} \mathcal{W}^n \right) - \rho \beta c^n g
\]

\[
\nabla \cdot v^n = 0.
\]

using a staggered **finite-volume** fluctuating hydrodynamics solver.

2. Do a **predictor advection-diffusion solve** for concentration,

\[
\frac{\tilde{c}^{n+1} - c^n}{\Delta t} = -v^n \cdot \nabla c^n + \chi_0 \nabla^2 \left( \frac{c^n + \tilde{c}^{n+1}}{2} \right).
\]
contd.

1. Solve a **corrector** steady Stokes system for **velocity**,

\[
\nabla \pi^{n+\frac{1}{2}} = \eta \left( \nabla^2 \mathbf{v}^{n+\frac{1}{2}} \right) + \nabla \cdot \left( \sqrt{\frac{2\eta k_B T}{\Delta t \Delta V}} \mathbf{W}^n \right) - \rho \beta \left( \frac{c^n + \tilde{c}^{n+1}}{2} \right) g
\]

\[
\nabla \cdot \mathbf{v}^{n+\frac{1}{2}} = 0.
\]

2. Take a **corrector** step for **concentration**,

\[
\frac{c^{n+1} - c^n}{\Delta t} = -\mathbf{v}^{n+\frac{1}{2}} \cdot \nabla \left( \frac{c^n + \tilde{c}^{n+1}}{2} \right) + \chi_0 \nabla^2 \left( \frac{c^n + c^{n+1}}{2} \right).
\]

This overdamped integrator provides a speedup of $O(\text{Sc})$ over direct integration of the original inertial equations.
Comparison to GRADFLEX transient

Figure: Qualitative theory [2]: $S(k, t) \propto [1 - \exp(-2Dk^2 t)]S(k, \infty)$
Relaxation times in confinement

Figure: Dimensionless effective decay times $\tilde{\tau}$ as a function of dimensionless wave number $\tilde{q}$ [3]. Filled red markers are experimental data, open blue are for calculations based on the FHD model, and open-dotted black are from numerical simulations.
Figure: The overdamped limit is only good for wavenumbers above $50\text{cm}^{-1}$. At even larger scales **fluid inertia cannot be neglected** when there is gravity present.
Propagative Modes

**Figure**: (Color online) Propagative modes (gravity waves) [1] appear in the inertial equations (dotted), but not overdamped (dashed).
Complex Fluids

We have generalized the models and numerical codes to include more complex fluids:

- **Multispecies mixtures** with complete transport including *thermo and barodiffusion* and boundary conditions and gravity [4]. We have simulated the development of gravity-driven diffusive instabilities and compared to experiments.

- **Chemically-reacting mixtures** [5]. We have studied giant fluctuations in reactive mixtures and found that the nonlinearity of the base (macroscopic) state is crucial and not yet captured in theory.

- **Multiphase liquids** including liquid-vapor coexistence [6]. We have simulated capillary waves, spinodal decomposition, condensation, and the piston effect.

- **Ionic mixtures** including electrostatic effects at length scales comparable to the Debye length (in preparation).
The species density equations for a mixture of $N_S$ species are given by

$$\frac{\partial}{\partial t} (\rho_s) + \nabla \cdot (\rho_s \mathbf{v} + \mathbf{F}) = m_s \Omega_s, \quad (s = 1, \ldots N_S) \quad (7)$$

Due to mass conservation $\rho = \sum_s \rho_s$ follows the continuity equation,

$$\frac{\partial}{\partial t} \rho + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (8)$$

The mass fluxes take the form, excluding barodiffusion and thermodiffusion,

$$\mathbf{F} = \rho \mathbf{W} \left[ \chi \Gamma \nabla \mathbf{x} + \sqrt{\frac{2}{n}} \chi^{\frac{1}{2}} \mathbf{W} F (\mathbf{r}, t) \right],$$

where $n$ is the number density, $x_s$ is the mole fraction of species $s$, and $\mathbf{W} = \text{Diag} \{ w_s = \rho_s / \rho \}$ contains the mass fractions.
\( \Gamma \) is a matrix of thermodynamic factors, 

\[
\Gamma = I + (X - xx^T) \left( \frac{\partial^2 g_{\text{ex}}}{\partial x^2} \right),
\]

where \( g_{\text{ex}}(x, T, P) \) is the normalized excess Gibbs energy density per particle.

\( \chi \) is an SPD diffusion tensor that can be related to the Maxwell-Stefan diffusion coefficients and Green-Kubo type formulas.

We, however, do not know values of these for even a single ternary mixture!

We have studied ideal mixtures: hard-sphere gas mixtures [7] and dilute solutions of salt+sugar in water [4].
Consider a system with $N_R$ elementary reactions with reaction $r$

$$\mathcal{R}_r : \sum_{s=1}^{N_S} \nu_{sr}^+ M_s \rightleftharpoons \sum_{s=1}^{N_S} \nu_{sr}^- M_s$$

The stoichiometric coefficients are $\nu_{sr} = \nu_{sr}^- - \nu_{sr}^+$ and mass conservation requires that $\sum_s \nu_{sr} m_r = 0$.

Define the dimensionless chemical affinity

$$\mathcal{A}_r = \sum_s \nu_{sr}^+ \hat{\mu}_s - \sum_s \nu_{sr}^- \hat{\mu}_s,$$

where $\hat{\mu}_s = m_s \mu_s / k_B T$ is the dimensionless chemical potential per particle.

Also define the thermodynamic driving force

$$\hat{\mathcal{A}}_r = \exp \left( \sum_s \nu_{sr}^+ \hat{\mu}_s \right) - \exp \left( \sum_s \nu_{sr}^- \hat{\mu}_s \right) = \prod_s e^{\nu_{sr}^+ \hat{\mu}_s} - \prod_s e^{\nu_{sr}^- \hat{\mu}_s}$$
The mass production due to chemistry can be approximated by the chemical Langevin equation (CLE) [5]:

\[
\Omega_s = \sum_r \nu_{sr} \left( \frac{P}{\tau_r k_B T} \right) \hat{A}_r + \sum_r \nu_{sr} \left( \frac{P}{\tau_r k_B T} \prod_s e^{\nu_{sr} \hat{\mu}_s} \right)^{\frac{1}{2}} \mathcal{Z}(r, t)
\]  

(9)

The CLE follows from a truncation of the Kramers-Moyal expansion at second order.

No true thermodynamic equilibrium since it assumes one-way reactions.

The CLE is not time-reversible (obeys detailed balance) at thermodynamic equilibrium wrt to the Einstein distribution. Proper description of chemical reactions requires the use of SDEs driven by Poisson noise (not Gaussian).
We have studied the Baras-Pearson-Mansour (BPM) model
\[ \mathcal{M} = (U, V, W, S, U_f, V_f), \]

\[ \begin{align*}
R_1 & : & U + W & \rightleftharpoons V + W \\
R_2 & : & V + V & \rightleftharpoons W + S \\
R_3 & : & V & \rightleftharpoons S \\
R_4 & : & U & \rightleftharpoons U_f \\
R_5 & : & V & \rightleftharpoons V_f
\end{align*} \] (10)

This system can exhibit limit cycles, bimodal states (bistability), and possibly other nonlinear behavior.
In principle this system can be simulated using particle methods!
Fluctuations change the dynamics qualitatively in spatially-extended reactive systems! How do we simulate this?
We will use a **diffusive-interface model** for describing interfaces between two distinct phases such as liquid and vapor of a single species.

Coarse-grained free energy follows the usual **square-gradient surface tension model**

\[
F (\rho(r), \nabla \rho(r), T(r)) = \int d\mathbf{r} \left( f (\rho(r), T(r)) + \frac{1}{2} \kappa |\nabla \rho(r)|^2 \right) \quad (11)
\]

The **local free energy density** \( f (\rho(r), T(r)) \) includes the hard-core repulsions as well as the short-range attractions.

Assume a **van der Waals** loop for the equation of state,

\[
P (\rho, T) = \frac{n k_B T}{1 - b' n} - a' n^2, \quad (12)
\]

\[
f = n k_B T \ln \left[ \frac{\rho}{1 - b' n} \right] - a' n^2.
\]
\[ \partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0 \] (13)

\[ \partial_t (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \mathbf{v}^T) + \nabla \cdot \Pi \equiv \nabla \cdot (\sigma + \Sigma) \] (14)

\[ \partial_t (\rho E) + \nabla \cdot (\rho E \mathbf{v} + \Pi \cdot \mathbf{v}) = \nabla \cdot (\psi + \Psi) + \nabla \cdot ((\sigma + \Sigma) \cdot \mathbf{v}), \] (15)

where the momentum density is \( \mathbf{g} = \rho \mathbf{v} \) and the total local energy density is \( \rho E = \frac{1}{2} \rho \mathbf{v}^2 + \rho e \).
Momentum Fluxes

- The reversible contribution to the stress tensor is [6]

\[ \Pi = P \mathbf{I} - \left[ \left( \kappa \rho \nabla^2 \rho + \frac{1}{2} \kappa |\nabla \rho|^2 \right) \mathbf{I} \right] - (\kappa \nabla \rho \otimes \nabla \rho) + \text{cross term?} \]

- Irreversible contribution to the stress is the viscous stress tensor

\[ \sigma = \eta \left( \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right) + \left( \zeta - \frac{2}{3} \eta \right) (\nabla \cdot \mathbf{v}) \mathbf{I} \quad (16) \]

- Stochastic stress tensor obeys fluctuation-dissipation balance

\[ \Sigma = \sqrt{2\eta k_B T} \tilde{\mathbf{W}} + \left( \sqrt{\frac{\zeta k_B T}{3}} - \sqrt{\frac{2\eta k_B T}{3}} \right) \text{Tr} \left( \tilde{\mathbf{W}} \right) \mathbf{I}, \quad (17) \]

where \( \tilde{\mathbf{W}} = (\mathbf{W} + \mathbf{W}^T)/\sqrt{2} \) is a symmetric white-noise tensor field.
Variance of height fluctuations versus wavenumber comparing 2D simulations (red circles) and capillary wave theory (CWT) (black solid line).
Spinodal decomposition in a near-critical Argon system at $\rho = 0.416 \text{ g/cc}$, $T = 145.85 \text{ K}$ leading to a **bicontinuous pattern**.
Condensation

Liquid-vapor spinodal decomposition in a near-critical van der Waals Argon system at $\rho = 0.36 \text{ g/cc}$, $T = 145.85 \text{ K}$ leading to **droplets** forming in a majority vapor phase.
S. Delong, Y. Sun, B. E. Griffith, E. Vanden-Eijnden, and A. Donev.
Multiscale temporal integrators for fluctuating hydrodynamics.
Software available at https://github.com/stochasticHydroTools/MixingIBAMR.

A. Donev, R. Cerbino, Y. Sun, and A. Vailati.
Dynamic scaling for the growth of non-equilibrium fluctuations during thermophoretic diffusion in microgravity.
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C. Giraudet, H. Bataller, Y. Sun, A. Donev, J. M. Ortiz de Zárate, and F. Croccolo.
Slowing-down of non-equilibrium concentration fluctuations in confinement.
Software available at https://github.com/stochasticHydroTools/MixingIBAMR.

Low Mach Number Fluctuating Hydrodynamics of Multispecies Liquid Mixtures.

Fluctuating hydrodynamics of multicomponent reactive mixtures.

A. Chaudhri, J. B. Bell, A. L. Garcia, and A. Donev.
Modeling multiphase flow using fluctuating hydrodynamics.

Fluctuating hydrodynamics of multispecies nonreactive mixtures.