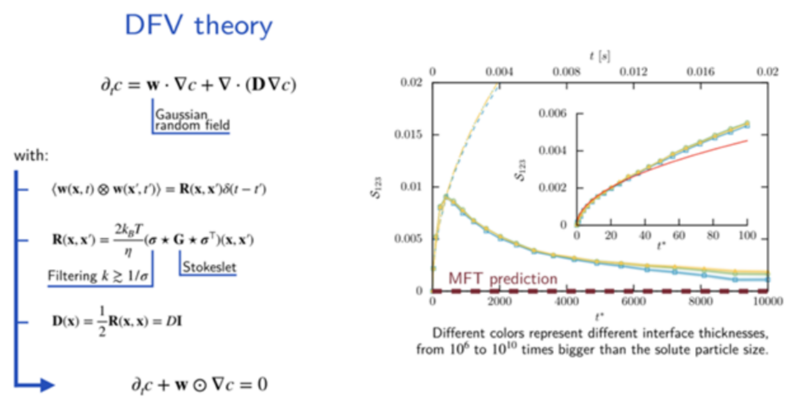
Non-Gaussian statistics of concentration fluctuations in free liquid diffusion

Marco Bussoletti[1], Mirko Gallo[1], Amir Jafari[2], Gregory Eyink[2]
[1]Sapienza University Of Rome, Rome, Italy, [2]The Johns Hopkins University, Baltimore, USA



The origin of macroscopic hydrodynamics from microscopic molecular dynamics has stimulated many different proposals, ranging from Mori-Zwanzig coarse-graining methods to effective field theories and macroscopic fluctuation theory (MFT) [1]. The universal validity of these approaches has further been challenged by the discovery of generic long-range correlations in non-equilibrium conditions. For instance, the giant concentration fluctuations observed during the free liquid diffusion of a binary mixture [2] have been interpreted in MFT as central limit theorem corrections to a leading-order law of large numbers [1]. This amounts to predicting Gaussian statistics in generic diffusive systems in the limit of small mean concentration gradients. Accordingly, the scaling of the non-equilibrium concentration correlations is also predicted by the linearized Landau-Lifshitz fluctuating hydrodynamics [2]. Therefore, non-equilibrium concentration fluctuations are widely expected to be Gaussian.

Based on the high Schmidt number limit of the nonlinear Landau-Lifshitz fluctuating hydrodynamics (FH) equations, Donev, Fai, and Vanden-Eijnden (DFV) interpreted the concentration fluctuations in a binary liquid at rest as the result of the nonlinear advection of solute concentration by a velocity field governed by thermal fluctuations [3] (see equations on the left of Figure 1). Their theory predicts the correct value of the renormalized diffusivity and explains Fickian diffusion as the mean behavior of the solute concentration at the macroscopic scale. Recently, by exploiting similarities between the DFV theory and the Kraichnan model for the turbulent advection of a passive scalar, we have asymptotically and numerically demonstrated that the DFV theory can also predict the correct non-equilibrium long-range correlations [4,5]. Besides, this analogy with turbulent transport suggests that concentration fluctuations may have richer statistics compared to what is prescribed by MFT and linearized FH.

In this talk, we establish this non-Gaussian nature. In particular, we exploit the DFV theory both analytically and by a massively parallel Lagrangian Monte Carlo simulation to show that the three-point skewness of concentration fluctuations is non-vanishing in free liquid diffusion, even in the limit of vanishingly small mean concentration gradients [6] (see plot on the right of Figure 1). The non-Gaussian statistics result from the nonlinear coupling of concentration fluctuations to thermal velocity fluctuations, analogous to the turbulent advection of a passive scalar. Ultimately, our results expose a direct discrepancy between nonlinear fluctuating hydrodynamics and macroscopic fluctuation theory, posing a conundrum that now awaits experimental resolution.

References:
[1] Bertini et al., Reviews of Modern Physics, 2015.
[2] Vailati et al., Nature, 1997.
[3] Donev et al., Journal of Statistical Mechanics: Theory and Experiment, 2014.
[4] Eyink et al., Annales Henri Poincaré, 2024.
[5] Bussoletti et al., The Journal of chemical physics, 2025.
[6] Bussoletti et al., Physical Review Research, 2026.