

A Reversible Mesoscopic Model of Diffusion in Liquids: from Giant Fluctuations to Fick's Law

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Diffusion is one of the most ubiquitous transport processes and is often thought to be one of the simplest dissipative mechanisms. Fick's law of diffusion is derived in most elementary textbooks, and relates diffusive fluxes to the gradient of chemical potentials via a diffusion coefficient that is typically thought of as an independent material property. In this talk we will discuss the microscopic and mesoscopic mechanism of diffusion in liquids, for both molecular diffusion and diffusion of colloidal particles. Through a combination of theory and simulations I will demonstrate that diffusion in liquids is, in fact, a rather subtle process due to the crucial contribution of hydrodynamic momentum fluctuations. Using multiscale analysis we derive a closed form stochastic diffusion equation that captures both Fick's law for the ensemble-averaged mean and also the long-range correlated giant fluctuations in individual realizations of the mixing process. These giant fluctuations, observed in experiments, are shown to be the result of the long-ranged hydrodynamic correlations among the diffusing particles. Through numerical experiments we demonstrate that mass transport in liquids can be modeled at all scales, from the microscopic to the macroscopic, not as irreversible Fickian diffusion, but rather, as reversible random advection by thermal velocity fluctuations. Our model gives effective dissipation with a diffusion coefficient that is not a material constant as its value depends on the scale of observation. We also use computer simulations to study the static and dynamic spectrum of concentration fluctuations in confined systems and compare to experimental results and simple (linearized fluctuating hydrodynamics) theories. We study both transient dynamics in the GRADFLEX experiment, performed in microgravity, as well as experiments performed on Earth, where gravity plays a key role.