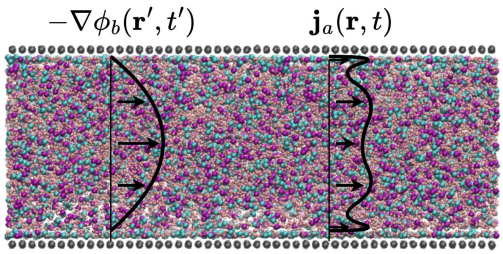
Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.28402

Faraday Discuss. 246, 198-224

Space- and time-dependent Onsager matrix in confined fluids: Bridging molecular interactions with coupled transport

MINH-THE HOANG NGOC AND IAN C. BOURG
Princeton University



$$\mathbf{j}_a(\mathbf{r},t) = -\sum_b \iint \mathbf{K}_{ab}(\mathbf{r},t;\mathbf{r}',t') \cdot \nabla\phi_b(\mathbf{r}',t')\,\mathrm{d}\mathbf{r}'\mathrm{d}t'$$

Understanding the microscopic interplay among mass, solute, heat, and charge transport at interfaces is essential for unravelling key geophysical processes. These insights have broad implications across environmental sciences—ranging from water and soil management[1], urban organization, and CO_2 sequestration to advanced applications[2] such as nanopore technologies, water desalination, or energy storage. Although continuum descriptions of transport perform well over a broad spectrum, thermal fluctuations, adsorption effects, electrical double layers, and molecular friction critically govern the richness of coupled phenomena at the nanoscale[3,4] and require atomistic considerations[5].

In this work, we introduce a unified methodology that leverages a space- and time-dependent response matrix to probe the intricate dynamics of confined fluids. Our formalism is summarized by the relation: [see figure and equation], where $j_a(r,t)$ denotes the local fluxes of: fluid, solute, heat, and charge, $\nabla\phi_b(r',t')$ the gradients of the conjugate driving potentials (*i.e.*, pressure, chemical potential, temperature, and electric potential), and $K_{ab}(r,t;r',t')$ the coupled response kernel accounting for non-local and memory effects. Using equilibrium molecular dynamics simulations on model confined fluids, we extend the Green–Kubo formulae[6] to sample the response kernel and connect microscopic mechanisms to the coupled responses.

This approach enables the dissection of fundamental processes—such as molecular layering, advection/diffusion of solutes and heat, and charge relaxation—and examines how confinement, salt concentration, and surface interactions modulate couplings (*e.g.,* thermo-hydraulic, hydro-electric, electro-osmotic etc...). The comprehensive space-time response framework bridges molecular behaviour with hydrodynamic theories, thereby advancing our understanding of transport at the nanoscale. The insights gained contribute to a deeper comprehension of solid-fluid interfaces, with significant implications for geophysics, electrochemistry, and various technological applications.

[1] : Hillel D. (2004), Introduction to Environmental Soil Physics, Academic Press

[2] : Bocquet L. (2020), Nature materials 19, 254–256

[3] : Wild B., White C.E., Bourg I.C. (2022), J. Phys. Chem. C 126, 9161-9172

[4] : Helms P., Poggioli R. P., Limmer T.L. (2023), Nano Lett. 23, 4226−4233

[5] : Kavokine N., Netz R.R., Bocquet. L. (2021), Annual Review of Fluid Mechanics 53(1):377–410

[6] : Hoang Ngoc M.T., Kim J., Pireddu G., Chubak I., Nair S., Rotenberg B. (2023),