Internship proposal

Laboratory: **Laboratoire de Physique de l'ENS** (LPENS, UMR 8023), **Micromegas** team
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Internship location: **ENS, 24 rue Lhomond, Paris 5ème**
Level: **M1 or M2** Thesis possibility after internship: **YES** Funding: **YES**

Critical flows: osmotic transport in liquids on the verge of demixing

In 1748, the abbé Nollet reported the first recorded observation of osmosis [1]. Almost three centuries later, osmosis still holds surprises, especially at the nanoscale. When a solute concentration gradient runs along a solid wall, the solute interacts with the wall within a thin interfacial layer. This creates a local osmotic pressure gradient that sets the liquid in motion: this is *diffusio-osmosis* [2]. In nanopores it produces giant osmotic currents [3, 4], which our team uses to harvest energy from salinity gradients (blue energy).

A recent idea is to use it to recover low-grade waste heat [5] (Fig. 1a). A mixture of water and an ionic liquid demixes when heated above about 30 °C. Mild heating thus splits the liquid into two phases of different salinity, which are then mixed back across a nanoporous membrane, generating a diffusio-osmotic current. But the experiments also revealed something unexpected: in concentrated mixtures, the osmotic current varies non-monotonically with the concentration ratio, and can even change sign. Standard diffusio-osmosis theory, built for dilute salts, cannot explain this.

What changes close to a demixing point? The thickness of the interfacial layer is no longer set by molecular sizes, but by the correlation length ξ of composition fluctuations, which diverges at the critical temperature T_c [6]. A few degrees could then tune the flow by orders of magnitude. Our recent theoretical work [7] suggests that the story is subtler, and more interesting (Fig. 1c): the critical enhancement depends strongly on the compositions of the reservoirs, and in pores narrower than ξ, where the two interfacial layers overlap (Fig. 1b), confinement changes which physics controls the flow.

None of these predictions has been tested experimentally.

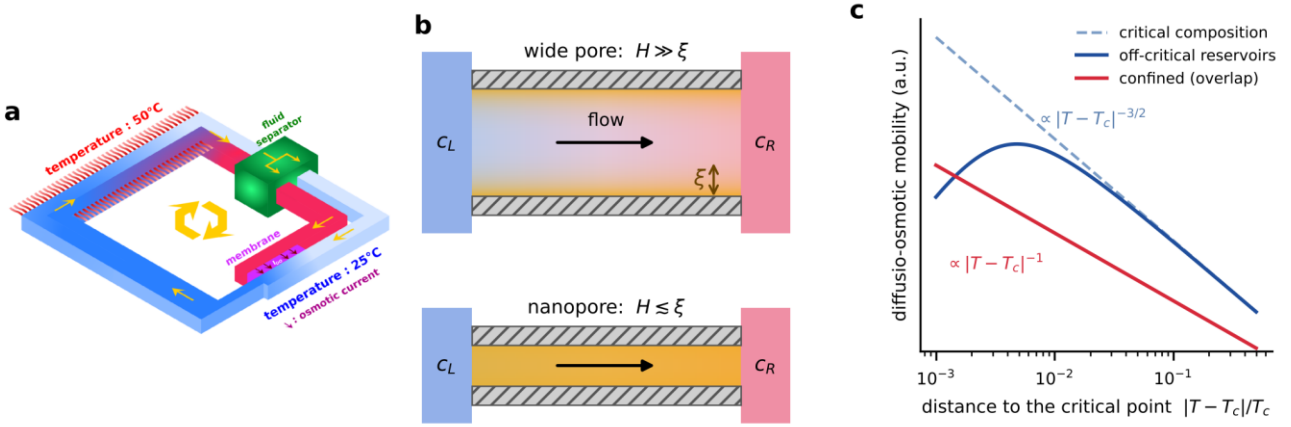


Figure 1. (a) Closed-loop waste-heat recovery with a thermoresponsive ionic liquid: heating separates the mixture into two phases of different salinity, which generate a diffusio-osmotic current when they meet again across a nanoporous membrane (adapted from [5]). **(b)** Near T_c, the interfacial layer that drives the flow (orange) grows with the correlation length ξ. In a wide pore the two layers are distinct; in a nanopore they overlap. **(c)** Predicted diffusio-osmotic mobility as the temperature approaches T_c [7].

The goal of this internship is to measure diffusio-osmosis close to a liquid–liquid critical point for the first time, and to put these predictions to the test. The intern will first characterise a thermoresponsive mixture near its critical point, such as water–$[P_{4444}][CF_3CO_2]$, or a neutral mixture such as water–2,6-lutidine. They will then measure diffusio-osmotic transport through nanopores and nanochannels under a controlled concentration gradient, using the ionic-current and flow measurements developed in the team, while bringing the temperature towards T_c. Varying the pore size and the reservoir compositions should reveal how composition and

confinement control the flow. Depending on their taste, the intern can also compare the data with the theoretical predictions and contribute to extending the model.

The project is mainly experimental, with a theoretical component. It sits at the crossroads of nanofluidics, critical phenomena and soft matter, and is well suited to a student who enjoys statistical physics and wants to see it at work in the lab. No previous experience in nanofluidics is required. Funding is secured for a PhD continuing this project after the internship.

[1] J.-A. Nollet, *Recherches sur les causes du bouillonnement des liquides*, Hist. Acad. R. Sci. (Paris, 1752), 57–104.
[2] J. L. Anderson, *Annu. Rev. Fluid Mech.* **21**, 61 (1989).
[3] A. Siria *et al.*, *Nature* **494**, 455 (2013).
[4] S. Marbach, L. Bocquet, *Chem. Soc. Rev.* **48**, 3102 (2019).
[5] M. Pascual, N. Chapuis, S. Abdelghani-Idrissi, M.-C. Jullien, A. Siria, L. Bocquet, *Energy Environ. Sci.* **16**, 4539 (2023).
[6] J. W. Cahn, *J. Chem. Phys.* **66**, 3667 (1977).
[7] C. Herrero, L. Bocquet, in preparation.