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Nanofluidic transport
Hydrodynamics beyond the wall

Baptiste Coquinot¹, Nikita Kavokine^{2,3*}

¹*École Normale Supérieure, Paris, France*

²*Max Planck Institute for Polymer Research, Mainz, Germany*

³*Flatiron Institute, New York, USA*

Contact: nkavokine@flatironinstitute.org

Nanoscale liquid-electron couplings affect water permeability through carbon nanotube porins.

In the study of fluid dynamics, walls are easily forgotten. A perfect hydrodynamic wall has no other property than being solid, thus providing a boundary for the fluid movements under scrutiny. The generic nature of walls is at the root of universality in hydrodynamics. For example, the permeability of a channel – the pressure one needs to apply to achieve a unit flow rate – is usually determined solely by the channel dimensions and the viscosity of the liquid being pushed through. Now writing in *Nature Materials*, Aleksandr Noy and coworkers report on a striking breakdown of the perfect wall approximation, as they find that the water permeability of tiny carbon nanotubes depends on their electronic nature [1].

The researchers relied on the well-established carbon nanotube porin (CNTP) platform [2]. Although introduced seven years ago, CNTPs have not exhausted the potential for surprising experimental results. They prepared tiny carbon nanotubes (of about 10 nm in length and sub-nanometer in diameter) which spontaneously insert into lipid vesicles. They then applied an osmotic pressure difference across the vesicle membrane by adding sugar to the solution and monitored the rate of vesicle shrinkage through light scattering. Knowing the number of CNTPs per vesicle, they thus determined the hydrodynamic permeability of one CNTP.

Such permeability measurements were reported previously, but new in this work is the fact that the CNTPs were purified to have a precisely defined arrangement of their carbon atoms, or *chirality*. One can think of a carbon nanotube as a graphene sheet that has been rolled up around a given axis. The orientation of this axis defines the chirality and the electronic nature of the resulting nanotube: either metallic or semiconducting. The authors isolated metallic nanotubes with diameter 0.75 nm, and semiconducting nanotubes with diameter of either 0.76 nm or 0.81 nm.

Strikingly, the metallic CNTPs were found to have about 50% higher permeability than the semiconducting CNTPs, despite their nearly identical diameter (Fig. 1). Concurrently, the larger 0.81 nm semiconducting CNTPs exhibited the same permeability as the 0.75 nm semiconducting CNTPs. The conclusion is unescapable: in these tiny channels, it is not the extent of the opening, but rather the band gap of the wall material that determines the hydrodynamic permeability.

This observation is all the more surprising that the ionic conductance – the ion transport rate under a unit voltage drop – was found to be the same for all batches of CNTPs.

In order to rationalize their results, the authors examined how the CNTPs respond to the electric fields produced by the translocating molecules – that is, their polarizability. Indeed, there is growing evidence to suggest that carbon nanotubes polarize very strongly, screening the charge of a potassium ion even more efficiently than bulk water [3, 4]. To account for this property in the framework of classical molecular dynamics simulations, some of the authors have previously developed a specific polarizable force field [5]. Here, they used this force field to simulate an electrolyte confined in the CNTP. In close correlation with experiment, they found that a water molecule is stabilized more strongly by the tube polarization when the tube is metallic, while the polarization energy of an ion is largely independent of the tube's electronic nature.

But what is happening at the microscopic level? In fact, the force field is parametrized by two physical quantities: the radial and axial polarizability of the nanotube. The axial component is larger for metallic than for semiconducting tubes, while the radial component is independent of the bandgap value. What the simulations demonstrate, somewhat counterintuitively, is that the screening of a charge (an ion) inside the tube is determined by the radial polarizability, while the screening of a dipole (a water molecule) is determined by both polarizability components. This is in fact analogous to the screening properties of nanoscale slits, for which analytical results were obtained [6]. Finally, the very short length of the CNTPs implies that the transport properties are determined by entrance effects: essentially, the energy barrier faced by either an ion or a water molecule to enter the channel mouth. However, in the case of water, permeation through a tube is a collective process, and the precise link between polarization energy and permeability remains to be established.

Altogether, these results demonstrate that water permeation through CNTPs is at odds with the paradigm of hydrodynamics. For short channels, where most of the dissipation occurs at the entrances, the classical hydrodynamic prediction is Sampson's formula, stating that the permeability scales as the channel radius cubed [7]. Here, this scaling clearly breaks down, and dissipation is no longer determined solely by the fluid viscosity: it is sensitive to the electronic nature of the channel wall.

In our view, the results of Noy and coworkers are the most direct evidence so far of the hydrodynamic wall concept failing at the nanoscale. They join a growing body of work that speaks to the importance of the wall's internal degrees of freedom in nanoscale fluid transport. In particular, these are instrumental to the fluctuation-induced quantum friction phenomenon [8], and to the coupling of liquid flows to electric currents in the channel walls [9]. While the latter rely on the non-adiabatic character of the liquid-electron interaction (the electrons have a slight delay with respect to the liquid dynamics), the observations in the CNTPs appear to be explained by an adiabatic model. It would be of great interest to measure the permeability of longer carbon nanotubes, where most of the dissipation occurs inside the channel rather than at the entrances, so that non-adiabatic effects may come into play. This poses, however, a formidable experimental challenge.

Finally, the above calls for the consideration of the practical implications of nanoscale liquid-electron couplings. Can we engineer the electronic properties of a channel to make it permeable to a specific liquid? Can we modulate these properties to make chemically specific valves? To do nanoscale plumbing, one will soon need to learn quantum mechanics.

Competing interests

The authors declare no competing interests.

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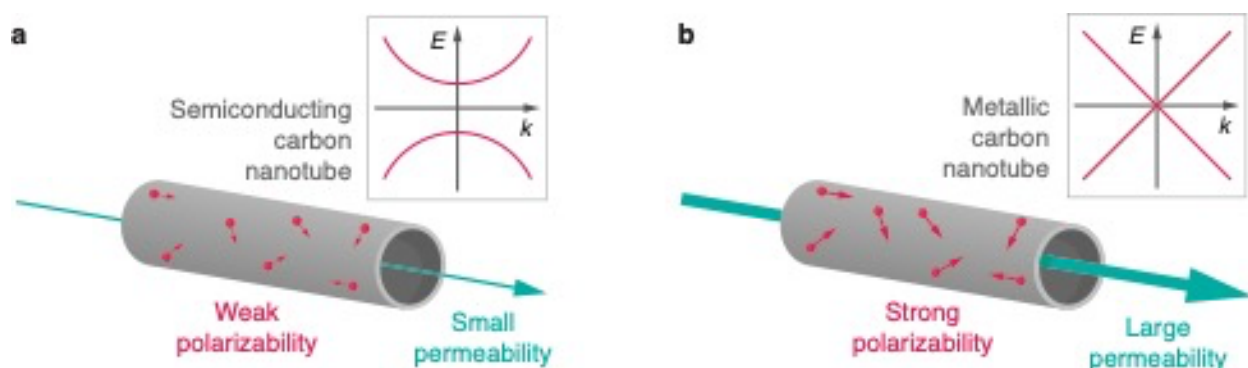


Figure 1. Illustration of the electronic nature of CNTs affecting their permeability to water. (a) The weakly polarizable semiconducting CNTs exhibit lower water permeability than (b) the strongly polarizable metallic CNTs. The insets show schematic representations of the CNTs' respective band structures.