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Reviewing the latest advances in microfluidic and nanofluidic research

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Nanofluidics, from bulk to interfaces†

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Nanofluidics has emerged recently in the footsteps of microfluidics, following the quest for scale reduction inherent to nanotechnologies. By definition, nanofluidics explores transport phenomena of fluids at nanometer scales. Why is the nanometer scale specific? What fluid properties are probed at nanometric scales? In other words, why does ‘nanofluidics’ deserve its own brand name? In this critical review, we will explore the vast manifold of length scales emerging for fluid behavior at the nanoscale, as well as the associated mechanisms and corresponding applications. We will in particular explore the interplay between bulk and interface phenomena. The limit of validity of the continuum approaches will be discussed, as well as the numerous surface induced effects occurring at these scales, from hydrodynamic slippage to the various electro-kinetic phenomena originating from the couplings between hydrodynamics and electrostatics. An enlightening analogy between ion transport in nanochannels and transport in doped semiconductors will be discussed (156 references).

I. Nanofluidics, surrounding the frame

Nanofluidics, the study of fluidic transport at nanometer scales, has emerged quite recently in the footsteps of microfluidics. Pushing the limits of fluidic downsizing further is an attractive goal, in the spirit of scale reduction inherent to all micro- and nano-technologies. Various reasons may be seen to motivate these novel developments. First, from the point of view of biotechnological (“lab on a chip”) applications, decreasing the scales considerably increases the sensitivity of analytic techniques, with the ultimate goal of isolating and studying individual macromolecules.1,2 But also, from the point of view of fluidic operations, nanometric scales allow new fluidic functionalities to be developed, using the explicit benefit of the predominance of surfaces. Typical examples involve preconcentration phenomena,3 the development of nanofluidic transistors4,5 or the recently proposed nanofluidic diodes.6,7 But the analogy to micro-electronics is somewhat limited: fluid molecules are not electrons and the notion of large scale integration for fluidic devices, i.e. nanofluidics as a way of increasing the density of fluidic operations on a chip even further, is probably not a pertinent goal to reach for fluidic operations.

But from a different perspective, nanofluidics also carries the hope that new properties will emerge by benefiting from the specific phenomena occurring at the smallest scales: new solutions may be obtained from the scales where the behavior of matter departs from common expectations. The great efficiency of biological nanopores (in terms of permeability or selectivity) is definitely a great motivation to foster research in this direction.8,9 There is indeed a lot of room for improvement at these smallest scales: the example of aquaporins (AQP) is interesting in this context. Aquaporin channels are a key component of many biological processes10 and play the role

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of water filters across biological membranes. These channels fulfill the conflicting tasks of being both extremely permeable to water, while extremely selective for other species. To give an order of magnitude, the permeability of the water channel is typically 3 orders of magnitude larger than what would be expected on the basis of the classical fluid framework for the same pore size. A potential answer is that AQP, although a filter for water, is mainly hydrophobic, i.e. water repellent! Of course some hydrophilic polar nodes are distributed along the pore, so as to keep water in the mainly hydrophobic environment. Quoting the terms of Sui et al. in ref. 8, "the availability of water-binding sites at these nodes reduces the energy barrier to water transport across this predominantly hydrophobic pathway, while the relatively low number of such sites keeps the degree of solute-pore interaction to a minimum. In balancing these opposing factors the aquaporins are able to transport water selectively while optimizing permeability." Beyond this elementary picture, understanding how AQP fulfills its challenging properties would definitely be a source of inspiration and open new perspectives for technological breakthrough in filtration, desalination, power conversion,… However reproducing such a delicate composite (patched) architecture in bio-mimetic membranes is a great challenge, which requires breakthrough in the conception of its elementary constituents. But it points out that surfaces and their chemical engineering are key to optimizing fluid properties at the nano-scale.

However, in its roots, nanofluidics is not a new field: as judiciously recalled by Eijkel and van den Berg in their pioneering review on the subject, many ‘old’ fields of physics, chemistry and biology already involve the behavior of fluids at the nanoscale. Like Monsieur Jourdain in “Le bourgeois gentilhomme” by Molière, one has done ‘nanofluidics’ for more than forty years without knowing it. One may cite for example the domains of electro-kinetics (electro-osmosis or -phoresis,…), photophysics, colloid chemistry, and of course physiology and the study of biological channels. An interesting question is accordingly whether—on the basis of the novel ‘nanofluidic’ point of view—one may go beyond the traditional knowledge in those ‘old’ fields and obtain unforeseen results, e.g. allowing for better optimization of existing technologies? Our belief is that the answer to this question is already positive and this is one of the key aspects that we shall discuss in this review.

Finally it is also important to note that nanofluidics has emerged recently as a scientific field (i.e. naming a field as “nanofluidics”) also because of the considerable progress made over the last two decades in developing nano-fabrication technologies, now allowing specifically designed nanofluidic devices to be fabricated, as well as the great development of new instruments and tools which give the possibility of investigating fluid behavior at the nanometer scale. One may cite for example: new electrical detection techniques, Surface Force Apparatus (SFA), Atomic Force Microscopy (AFM), nano-Particle Image Velocimetry (nano-PIV) coupling PIV to TIRF set-up (Total Internal Reflection Fluorescence), as well as the considerable progress made in computational techniques, like Molecular Dynamics simulations. It is now possible to control/design what is occurring at these scales, and observe/measure its effects. This is the novelty of the field, and the reason why nanofluidics now deserves its own terminology.

The paper is organized as follows: In the second section we will replace nanofluidics in the perspective of the various length scales at play in fluid dynamics. We shall in particular discuss the limits of validity of continuum (e.g. hydrodynamic) descriptions. In the third section we discuss the dynamics of fluids at interfaces and the nanofluidic tools which have been developed recently to investigate it. In the fourth section we will explore various transport phenomena occurring in diffuse layers. In the fifth section we will raise the question of thermal noise in nanofluidic transport. Finally we will conclude by exploring some general considerations and expectations about nanofluidics, especially in terms of energy conversion and desalination.

As a final remark, this review, like any review, is our subjective and personal view of the field of nanofluidics and the perspectives one may foresee. We organized our exploration around the length scales underlying fluid dynamics at the nanometric scales and how nanofluidics allows us to probe the corresponding mechanisms. Accordingly, our aim is not to explore exhaustively the—already large—literature of the domain, but merely to disentangle the various effects and length scales underlying the behavior of fluids at nanometer scales. In doing so, we certainly hope that this review will raise new questions, open new directions and attract people to this fascinating domain.

II. Limits of validity of continuum descriptions and nanofluidic length scales

The introduction of the terminology “nanofluidics” (furthermore to define a specific scientific field) suggests that something special should occur for the transport of a fluid when it is confined in a channel of nanometric size. This leads to an immediate question: why should the nanometer length scale have anything specific for fluidic transport? Nanofluidics “probe” the properties of fluids at the nanoscale: so, what does one probe specifically in the nanometer range?

Actually one may separate two different origins for finite-size effects associated with nanometer scales: bulk and surface finite-size effects. The former, bulk effects are intimately associated with the question of validity of the classical continuum framework, in particular the Navier–Stokes equations of hydrodynamics: when do such descriptions break down? Can one then expect ‘exotic’ fluid effects associated with the molecular nature of the fluid? On the other hand, surface
effects play an increasingly important role as the “surface to volume ratio” increases (i.e. as the confinement increases). We have already pointed out the importance of such effects on the example of AQP water channels. As we show below, the surface effects occur at much larger scales than the ‘bulk’ deviations from continuum expectations.

The discussion on the length scales at play, to be explored in this section, is summarized in Fig. 1.

A Validity of bulk hydrodynamics

We first start with a short discussion on the validity of bulk hydrodynamics. In practice, this raises the question: when do the Navier–Stokes (NS) equations break down? These equations were developed in the 19th century to describe fluid flows at, say, the human scale. What comes as a surprise is their incredible robustness when applied to ever smaller scales.

As a fact, for simple liquids, the continuum framework of hydrodynamics is apparently valid down to the nanometer scale. In other words, there is no expected deviation to the bulk NS equations for confinement larger than ~1 nm. This very surprising result is actually suggested by a number of experimental and molecular simulations studies. On the experimental side, one may cite the early work by Chan and Horn13 and later by Georges et al.14 using Surface Force Apparatus, where the prediction of hydrodynamics (the Reynolds formula in their case) was verified to be valid for confinement larger than typically ten molecular diameters. More recently, and specifically for water, the works by Klein et al.15 and E. Riedo et al.16 showed that water keeps its bulk viscosity down to ~1–2 nm, with a drastic change of behavior for stronger confinements, where the wettability of the confining surface plays a role.16 A similar behavior was found for other liquids like octamethylcyclotetrasiloxane (OMCTS).17,18

This threshold for the applicability of continuum hydrodynamics was also investigated using Molecular Dynamics simulations of confined water, and the same value of about 1 nm came out of the simulation results.19–21 Furthermore, it is interesting to note that beyond the validity of continuum equations, the value of the viscosity also remains quantitatively equal to its bulk value. We show in Fig. 2 the results of MD simulations for the viscosity η of water (SPC-E model) measured in various confines. The value of the viscosity is obtained by measuring the shear-stress on the confining plates for a given shear-rate (corrected for slippage effects). As shown in this figure, the shear viscosity of water keeps its bulk value down to confines of ~1 nm (typically 3 water layers).

Now, in contrast to the viscosity, other transport coefficients may be more strongly affected by confinement. This is the case for example of the (self-)diffusion coefficient which was shown to depend algebraically on the confinement width.22,23 As a consequence, the diffusion coefficient in confinement strongly departs from its Stokes–Einstein prediction, \( D = k_B T / (3 \pi \eta r) \), with \( r \) the molecule diameter. The latter is accordingly not a correct measure of the viscosity, as sometimes assumed.19,24

Fundamentally the validity of NS equations down to typically 1 nm (for water) is \textit{a priori} unexpected. Navier–Stokes (NS) equations have been developed to account for the fluid dynamics at ‘large’ scales and they rely on an assumption of a local and linear relationship between stress and velocity gradients.

To our knowledge, there is no firmly grounded argument for this validity and we propose here a few tentative leads. NS equations, like any continuum framework, rely actually on the key assumption of a separation of length- and time-scales between the investigated length scale and the ‘molecular’ dynamics. This is the “hydrodynamic limit”, in which the continuum framework should hold. Under this time- and length-scale separation, the microscopic dynamics associated with a huge number of degrees of freedom \( \mathcal{N} \approx 10^{23} \) reduces to equations with just a few degrees of freedom (velocity field, pressure, density, temperature, \textit{etc}.), while all the complexity is hidden in just a few phenomenological coefficients. Achieving this averaging out of the “fast variables” is a huge challenge which can be achieved systematically only in a few limiting cases, see e.g. ref. 25 for an explicit example. In general, the elimination of fast variables is summarized in the Green–Kubo relationship for the transport coefficients: for example the shear viscosity \( \eta \) can be expressed as the integral of the stress–stress correlation function according to

\[
\eta = \frac{1}{k_B T} \int_0^\infty \langle \sigma_{xy}(t) \sigma_{xy}(0) \rangle_{\text{equ}} \, dt
\]  

with \( \sigma_{xy} \) a non-diagonal component of the stress tensor26 and \( \langle \rangle_{\text{equ}} \) denotes an equilibrium average.

The time-scale separation underlying the validity of eqn (1) requires the microscopic time scales, \( \tau_\nu \) characterizing the stress–stress correlation function, to be much smaller than a hydrodynamic time scale. This time scale is e.g. the relaxation time of momentum, which for a given wave vector \( q \) has the expression \( \tau_\nu = (\nu q^2)^{-1} \), with \( \nu = \eta / \rho \) the kinematic viscosity and \( \rho \) the mass density. An implicit condition of validity is accordingly \( \nu q^2 \tau_\nu < 1 \). This fixes the limit for time-scale separation at confines \( w \) larger than a viscous length scale:

\[
w > \ell_c = \sqrt{\nu \cdot \tau_\nu}
\]
Putting numbers for water, a typical correlation time for the stress–stress correlation function is in the picosecond range $\tau_c \sim 10^{-12}$ s, while $\nu = 10^{-6}$ m$^2$ s$^{-1}$. Altogether this gives for water

$$\ell_c \approx 1 \text{ nm}$$

A nanometric characteristic length scale thus emerges naturally as a lower boundary for the validity of the notion of viscosity, and thus for the application of standard NS hydrodynamics. This is indeed the experimental value below which strong departure from the continuum framework is observed.

Of course, it would be interesting to explore further the physical contents of this condition: what occurs for smaller confinements? Also, can one tune $\ell_c$ in specific systems? etc.

In the extreme limit of single file transport, the transport behavior is indeed expected to strongly deviate from the bulk expectations, with the predicted occurrence of anomalous diffusion, and of fast stochastic transport, to cite some examples.28–30 Apart from biological systems—where molecular pores are the rule—fabricating channels with molecular size is however still out of reach with state-of-the-art nanofabrication technologies.

As a side remark, it would be interesting to extend this discussion to other transport phenomena, like for example heat transfer at nanoscales. Heat transfer from nanoparticles and nanostructures to a fluid is an actively growing field, e.g. in the context of cooling enhancement by structured surfaces or local heating of fluids via nanoparticles.27 Similar arguments as above may be proposed, and lead to an equivalent sub-nanometer heat length scale (for water at room temperature). This suggests that the continuum phenomenological picture for heat transport in fluids, involving Fourier law, is expected to hold down to nanoscales, in agreement with observations.27 However a full investigation of the limit of applicability of the corresponding continuum phenomenological laws remain to be developed in general.

A conclusion of the above discussion is that for most nanofluidic applications involving water in supra-nanometric confinements, bulk NS equations can be safely used to account for the fluid transport.

**B A broad spectrum of length scales**

Aside from $\ell_c$ introduced above, there are a number of length scales which enter nanofluidic transport. These length scales are all related to surface effects in one way or another. We review in this section a panel of these length scales, climbing up from the smallest—molecular—scales to the largest, but still nanometric, scales. This panel is not exhaustive, and we merely insist on the main length scales which appear generically in nanofluidic problems. Our aim is to show that there are a number of pertinent scales which lie indeed in the nanometric range. This implies that specific nanofluidic phenomena will show up when the confinement compares with these values.

1. **Molecular length scales.** At the smallest scales, the granularity of the fluid and its components (solvent, ions, dissolved species, . . .) should play a role. This is defined by the molecular scale, associated with the diameter of the molecules $\sigma$, typically in the Angström scale, 3 Å for water. As we discussed above, this is the scale where the validity of hydrodynamics breaks down, typically for confinements of 3–5 molecular diameter. Various phenomena then come into play. First, the structuring and ordering of the fluid at the confining walls plays a role. Such ordering was indeed shown experimentally to induce oscillatory dissipation in liquid films with a width of several molecules diameter.17,18

Similarly non-local rheological properties have been predicted in strongly confined situations,31 associated with a length characterizing non-locality typically in a few diameters range (indeed in line with the above limit of NS hydrodynamics). This result echoes recent findings of non-local flow curves in confined soft glasses.32 An interesting consequence of non-locality, as pointed out in ref. 32, is that the specific nature of surfaces does influence the global flow behavior in confinement, in line with recent observations in AFM measurements by Riedo et al. for strongly confined water (less than 1 nm) films at hydrophilic and hydrophobic surfaces.16

But even more drastic are the deviations occurring in the extreme limit where only one molecule can enter the confining pore. Very strong correlations and collective motion build up in the liquid dynamics, leading to the so-called “single-file” transport.33,34 The associated transport differs strongly from the bulk hydrodynamic predictions and various specific phenomena show up, like non-fickian transport,34 fast water transport and ion transfer, stochastic flow with the occurrence of “bursts”, etc., see e.g. ref. 33. Simulations of water transport through single-file carbon nanotubes (where only one water molecular can pass through the channel) showed indeed flow rates much larger than those predicted from the Poiseuille law of hydrodynamics.28

Note however that this behavior is limited to nanochannels where molecules cannot cross each other, i.e. with diameters not exceeding the water molecular length scale, like in biological channels. Up to now, artificially produced nanochannels do not reach this limit. This point is interesting to discuss in the context of recent experimental results obtained for flow through carbon nanotube membrane.35,36 A recent experimental first was achieved in Bakajin’s group, who investigated the flow through a membrane constituted of carbon nanotube with a size in the range 1.3–2 nm, following the work on larger nanotubes (~7 nm) by Majumder et al.37 These works demonstrated massively enhanced flow permeability, as compared to bulk predictions (in terms of slippage, to be discussed below, this would correspond to slip lengths up to a micron, far above any expected result for these surfaces). More recent experiments performed with membranes made of wider carbon nanotubes suggest a large, but still smaller, enhancement of the permeability.38 Therefore, while it would be tempting to discuss these results in the context of single-file transport and the predictions by Hummer et al. on fast single-file transport in sub-nanometer carbon nanotube,33 this point of view is difficult to justify: as discussed above, fluid flow in nanotube pipes with a supra-nanometric diameter can be safely described by continuum approaches (Stokes equation) and the dynamics is definitely not single file. Molecular Dynamics simulations of flow through similar carbon nanopipes indeed suggest large flow enhancement,24,35 but still far below the experimental results. There is therefore a strong need to perform flow
experiments through a single object, i.e. through a single carbon nanotube. This is still an experimental challenge.

Altogether transport at the molecular scale offers a rich panel of transport behavior. This is definitely the scale where, as we quoted in the introduction, new solutions and technological breakthrough could emerge as the behavior of matter departs from common expectations. This suggests that the molecular scale would be the ultimate scale to reach for nanofluidics. But at present, producing channels of sub-nanometric size remains a technological challenge.

2. Electrostatic length scales and their dynamic influence.

The scales associated with the interaction of the flowing matter with its environment also enter the game. And of course, electrostatics plays a key role in this context. We leave aside interactions deriving indirectly from electrostatics to focus on the interactions between charged species. These obviously concern ions dissolved in the fluid: ion–ion interactions, and interactions of ions with charged surfaces. This also involves the dipolar interaction among water molecules, as well as H-bonding.

Electrostatics involves a rich panel of length scales. And more importantly, due to the long range nature of electrostatics, these length scales are intimately coupled: effects occurring at the smallest electrostatic lengths do climb the scales to span the whole range.

a. Bjerrum length (and some derivatives). We start with the Bjerrum length, $\ell_B$, which is defined as the distance at which the electrostatic interaction $\psi_{el}$ between two charged species becomes of the order of the thermal energy, $k_BT$: $\psi_{el}(\ell_B) \approx k_BT$. For two ions, with valence $Z$, embedded in a dielectric medium with dielectric constant $\epsilon$, this takes the form

$$
\ell_B = \frac{Ze^2}{4\pi\epsilon k_BT}
$$

(e the elementary charge). For bulk water at ambient temperature and a valency $Z = 1$, this gives $\ell_B = 0.7$ nm. The Bjerrum length therefore compares with the molecular range in this case. Note however that for multi-valent ions or for organic solvent with lower dielectric constants, $\ell_B$ may be much larger and thus separate from the molecular range.

Other length scales could be introduced along the same lines by comparing thermal energy to e.g. charge–dipole, dipole–dipole, etc. interactions, taking into account the multi-pole interaction under consideration. This leads a priori to length scales smaller than the Bjerrum length introduced above. For the charge–dipole interaction, this gives for example $\ell_d = (\ell_B^2)^{1/2}$, with $p$ the dipole strength: for water parameters, $\ell_d$ is in the Angstrom range. It does correspond to the typical thickness of a hydration layer around an ion.38

By definition, the Bjerrum length (and other Bjerrum-like lengths such as $\ell_d$ above) is the scale below which direct electrostatic interactions dominate over thermal effects. Its consequences on nanofluidic transport is thus expected at the molecular scale. For example, for confinement below $\ell_B$ one expects a large free-energy cost to undress an ion from its hydration layer and make it enter a molecular pore. This has therefore immediate consequences on the filtering process of charged species, as in biological ion channels.

But as pointed out above, a strong interplay with upper scales is expected due to the long range nature of electrostatic interactions. For example, as we will discuss in section IV, ion-specific effects at interfaces, the origin of which occurs at a scale $\ell_B$, have strong effects on the electro-kinetics at nanometric, micrometric and even larger scales.

b. Debye length scale. A central concept of electrostatics is the notion of the electrostatic diffuse layer (EDL). At a charged interface, the EDL is the region where the surface charge is balanced by the cloud of counterions. In this region the ion concentration profile depart from their bulk values due to the interaction of ions with the surface charge. This is therefore the region where local electro-neutrality is not obeyed.

The Debye length emerges naturally from the Poisson–Boltzmann theory and characterizes the electrostatic screening in the bulk electrolyte.39 It is defined in terms of the salt concentration $\rho_s$ according to the expression:

$$
\lambda_D = \left(\frac{8\pi \rho_s \epsilon_0 \epsilon}{k_B T}\right)^{1/2}
$$

(5)

Note that in this expression, as in the following, $\rho_s$ denotes the salt concentration in the reservoirs, thereby fixed by the chemical potential of the ions. The value of the Debye length depends on the salt concentration and ranges typically between tens of nanometers (30 nm for $\rho_s = 10^{-4}$ M) down to Angstroms (3 Å for $\rho_s = 1$ M). In physical terms, the electrostatic free-energy of an ion dressed by its spherical cloud of counterions with size $\lambda_D$ is of the order $k_BT$.

The Debye length characterizes the width of the EDL. Interestingly, it is independent of the surface charge and only depends on the bulk ion concentration. However, in the limiting case of a salt free solution (with $\lambda_D \to \infty$), the width of the diffuse layer is merely fixed by the so-called Gouy–Chapman length, to be defined in the next paragraph.

The Debye length plays a central role in nanofluidics for various reasons. First, as quoted above, this is the region in the fluid close to charged surfaces where local charge electro-neutrality is broken. Under an applied electric field, this is thus the region where volume electric forces, $f_v = \rho_s E_v$, will apply, with $\rho_s$ the charge density and $E_v$ an applied electric field. On the other hand these forces vanish in the bulk of the material due to a vanishing charge density $\rho_s \to 0$ far from the surfaces. Therefore tuning the fluid properties inside the nanometric EDL is expected to affect the whole response of the system under an electric field. Accordingly, tuning the dynamics of the fluid in the nanometric EDL, or modifying its structure, will have a macroscopic impact on the fluid dynamics at scales much larger than the Debye length. We will return extensively to this question below, in section IV.B.

Second, a specific behavior is expected when the Debye layers overlap in a nanopore, which occurs when its size is of the order of twice the Debye length. This phenomenon has a strong effect on fluidic transport and has been the object of intense research recently, as reviewed recently by Schoch et al.40 see section IV. One may cite in particular the phenomena of ion enrichment and exclusion.2 While these phenomena were known for a long while in membrane technology, they found
new applications in the field of nanofluidics. It is at the root of a number of novel fluidic phenomena, such as permselectivity, nanofluidic diodes or surface dominated ion transport. A key practical aspect is that the condition of Debye layer overlap is much less stringent to fulfill with actual nanofabrication techniques. These are now able to produce individual nanopores with at least one dimension in the range of ten nanometers, i.e. potentially suited for Debye layer overlap.

c. Length scales associated with surface charge: Gouy-Chapman and Dukhin. Other electrostatic length scales may be constructed on the basis of surface electrostatic properties. We have already mentioned the Gouy-Chapman length scale, which shows up for the behavior of a salt solution very close to a charged surface. For a surface charge density \( \sigma \), this has an expression \( \ell_{GC} = 1/(2\pi \Sigma \sqrt{\lambda_D}) \). In contrast to the Debye length, the Gouy-Chapman length depends explicitly on the surface density \( \Sigma \) of charges of the confining surface (\( \Sigma \) in units of \( \text{m}^{-2} \)), but not on the bulk ion concentration. Physically, the Gouy-Chapman length can be defined as the distance from the wall where the electrostatic interaction of a single ion with the wall becomes of the order of the thermal energy. For typical surface charges, say \( \Sigma \approx 50 \text{ mC/m}^2 \) (i.e. \( 0.3 \text{ e/nm}^2 \)) to fix ideas, then \( \ell_{GC} \approx 1 \text{ nm} \). The Gouy-Chapman length plays a role for solutions with very small salt concentration. This has an influence on the conductance in nanochannels as we discuss in section IV C.

More interesting is a length which can be defined on the basis of the comparison between the bulk to the surface electric conductance (relating electric current to an applied electric field). This introduces what can be termed as a “Dukhin length”, by analogy to the Dukhin number usually introduced for colloids. Indeed the conduction probes the number of free carriers (ions), so that in a channel of width \( h \) and surface charge \( \Sigma \), the equivalent bulk concentration \( C_b \) of counterions is \( 2\Sigma /h \). One may define a Dukhin number \( Du = |\Sigma|/(h\rho_s) \), where \( \rho_s \) is the concentration of the salt reservoir. A ‘Dukhin length’ can then be defined as

\[
\ell_{Du} = \frac{|\Sigma|}{\rho_s}.
\]

To put in numbers, for a surface with a surface charge density \( \sigma \approx 50 \text{ mC/m}^2 \) (i.e. \( 0.3 \text{ e/nm}^2 \)), \( \ell_{Du} \) is typically 0.5 nm for \( \rho_s = 1 \text{ M} \), while \( \ell_{Du} = 5 \text{ nm} \) for \( \rho_s = 10^{-4} \text{ M} \). The Dukhin length characterizes the channel scale below which surface conduction dominates over the bulk one. In a different context of charge discontinuities at surfaces, it has also been interpreted in terms of an electrokinetic “healing” length.33

This length scale can actually be rewritten in terms of the Debye and Gouy-Chapman lengths as \( \ell_{Du} \approx \ell_D^2/\ell_{GC} \). Note also that in the limit where the Debye length is large compared to the Gouy-Chapmann length, \( \ell_{GC} < \ell_D \), the non-linear Poisson–Boltzmann expression for the electrostatic potential59 allows the above length to be rewritten as \( \ell_{Du} \approx \ell_D \exp(V_s/2k_BT) \), with \( V_s \) the surface potential. The corresponding form for the Dukhin number is more standard in colloid science.42

This length plays an important role for the conductance in nanochannels, cf. section IV C, where surface effects are shown to strongly affect conductance.41,44

3. Slip lengths and surface friction. Up to now we merely considered length scales characterizing the structure of the fluid and its components (ions, ...). However the dynamics of fluids at interfaces introduce various length scales. This is in particular the case of the so-called slip length, \( b \), characterizing the hydrodynamic boundary condition of a fluid at its confining interfaces. The latter is defined according to the Navier boundary condition (BC) as ref. 21

\[
b \partial_{\nu} v_r = v_t,
\]

with \( n, t \) points to the normal and tangential directions of the surface, \( v_t \) is the tangential velocity field and \( b \) the slip length. The slip length characterizes the friction of the fluid at the interface and large slip lengths are associated with low liquid–solid friction.

This point has been amply explored experimentally and theoretically: a key result which emerges from this measurements is that the slip length of water at solid surfaces depends crucially on the wettability of the surface.21,45 We will come back more exhaustively on this point in section III. At this level, one should keep in mind that slip lengths in the range of a few tens of nanometers are typically measured on hydrophobic surfaces, while \( b \) is sub-nanometric on hydrophilic surfaces. Note however that very large slip length, in the micron range, may be obtained on nano- and micro-structured interfaces.46,47

This offers the possibility to modify the nanofluidics in pores using chemical engineering of the surfaces. As the pore size compares with \( b \) a considerable enhancement of fluid transport is accordingly expected. Furthermore one may remark that these values of \( b \) also compare with typical Debye lengths. Therefore slippage effects are expected to affect ion transport at charged surfaces. We will discuss these aspects more exhaustively below.

A final remark is that other surface related lengths may be constructed. This is the case in particular of the Kapitza length, which characterizes the boundary condition for thermal transport across an interface, see e.g. ref. 21. The Kapitza length behaves quite similarly to the slip length and strongly depends on the wettability of the interface.48

4. Other length scales. The review of length scales above is not exhaustive and many other length scales may enter the game, depending on the problem, geometry and system considered. For example, in the context of transport of macromolecules (colloids, polymers, DNA, RNA, proteins, ...), the typical size of the particle—diameter or radius or gyration—plays of course a central role. More precisely a key quantity is the free energy associated with the confinement of the macromolecule, \( \mathcal{F}_s \), which fixes the partitioning of the molecule in the nanopore with respect to the bulk. The probability of the passage of a macromolecule through a pore is expected to scale like \( \exp[-\mathcal{F}_s/k_BT] \), hence fixing its permeability.49 For example for a polymer chain confined in a pore with size \( D \), the entropic cost of confinement takes the form \( \mathcal{F}_s \approx k_BT(R_g/D)^{1/2} \), with \( R_g = a \times N^2 \) the radius of gyration of the polymer (\( a \) the monomer size and \( N \) the polymer length). For a polymer in good solvent, the Flory exponent is \( \nu = 5/3 \). Pores the size of which is below the radius...
of gyration of the molecule thus act as a molecular sieve. This has been explored in various experiments of polymer translocation in nanopores following the pioneering work of Bezrukov et al.50,51 and Kasianowicz,52 as well as in the context of DNA separation.53

C Some practical conclusions

The discussion above is summarized in Fig. 1, where we organized the various scales at play along the scale axis. This points to several conclusions.

1. A number of specific phenomena occur in the nanometric range, which indeed justifies the specificity of the dynamics of fluids in the nanometer range, i.e. nanofluidics.

2. An important conclusion is: For water under normal conditions, the Navier–Stokes equation remains valid in nano-channels down to typically 1–2 nanometers. This is good and bad news. Good because one may safely use NS equations for most nanofluidic phenomena. This robustness of continuum hydrodynamics is remarkable.

But this is in some sense bad news since it means that reaching specific effects associated with the granularity of the fluid requires molecular confinement, i.e. confinement below the nanometer. Producing nano-channels with such sizes is technologically difficult to achieve. On the other hand, this probably explains why most biological channels have a molecular entanglement: to reach specificity and avoid the “universality” associated with continuum equations, one should reach the fluid molecular scale.

3. This suggests that the molecular pore is the ultimate scale to reach for nanofluidics, where, as we quoted in the introduction, new solutions and technological breakthrough could emerge as the behavior of matter departs from the common expectations. But at present, there is however still a long way before this scale is technologically accessible.

4. While it remains difficult to tune the bulk behavior of the confined fluid, there is much more room and possibilities to benefit from surface effects. This is clearly apparent in Fig. 1, where surface effects enter the nanofluidic game at much larger length scales. Surface effects enter in particular via the Debye length, Dukhin length, slip length, all typically in the ten nanometer range (and even more for the Dukhin length). This suggests that specific effects will show up when one of these lengths will compare with the pore width. Furthermore, particular effects should also occur when two of these lengths become comparable, independently of the confinement. This will be explored in section IV.

Altogether nanofluidics is an incredible playground to play with surface effects!

III. Dynamics at surfaces and the toolbox of nanofluidics

We have discussed above that the bulk laws of hydrodynamics are valid down to very small scales, typically ~1 nm, so that bulk Navier–Stokes equations can be used for most nanofluidic flows. However as the size of the nanochannel decreases, the dynamics at its surface should play an increasingly important role. Navier–Stokes equations require boundary conditions (BC) for the hydrodynamic flow at the device’s surface, and a specific knowledge of these BC is a prerequisite to apprehend flow at the nanoscale.

As quoted in eqn (7), the BC at a solid surface introduces a new length, the so-called Navier length or slip length, which relates the tangential velocity \( v_t \) to the shear rate at the wall, Fig. 3.54

\[
\frac{v_t}{\gamma} = b \frac{\partial v_t}{\partial z} \tag{8}
\]

Obviously the control of the slip length is of major importance for flows in confined geometries, and it can have dramatic consequences on the pressure drop, electrical, and diffusive transport through nanochannels. For instance the relative increase in hydraulic conductance of a cylinder of radius \( r \) due to wall slippage is \( 1 + 8b/r \); it can be much larger for the electrical conductance or electro-osmosis, as we will discuss in the sections below.

As a consequence a sustained interest has been devoted in the last ten years for the investigation of the BC and its dependence on interfacial properties, such as surface topography and liquid–solid interactions. Reviews on this subject can be found in ref. 21, 55 and 56.

A Theoretical expectations for slippage

The theoretical understanding of slippage has been the object of intense research over the last decade, see ref. 21 for a review. The BC has been studied theoretically by Molecular Dynamics simulations, as well as in the context of linear response theory.45,57–61 It is now well understood that the BC on atomically smooth surfaces depends essentially on the structure of the liquid at the interface, itself determined by its interactions, its commensurability with the solid phase, and its global density.21

In order to connect the slip length to the interfacial properties, it is useful to interpret the slip length in terms of liquid–solid friction at the interface. The friction force at the liquid–solid interface is linear in slip velocity \( v_t \):

\[
F_f = -\lambda v_t \tag{9}
\]

with \( \lambda \) the liquid–solid friction coefficient and \( \mathcal{A} \) the lateral area. By definition the slip length is related to the friction
coefficient according to \( \lambda = \frac{\eta}{\mu} \), with \( \eta \) the bulk viscosity. As a phenomenological friction coefficient, \( \lambda \) can be expressed in terms of equilibrium properties in the form of a Green–Kubo (GK) relationship:\(^{21,59,62}\)

\[
\lambda = \frac{1}{\sqrt{2}\kappa T} \int_0^\infty \langle F_f(t) \cdot F_f(0) \rangle_{\text{equ}} \, dt \tag{10}
\]

where \( F_f \) is the total (microscopic) lateral force acting on the surface. In practice, this expression is difficult to estimate. However some useful information on the slip length may be extracted from it.

A rough estimate of slippage effects can be proposed.\(^{63}\) One may indeed approximate the GK expression as

\[
\lambda \approx \frac{1}{\sqrt{2}\kappa T} \langle F_f^2 \rangle_{\text{equ}} \times \tau, \quad \text{with } \tau \text{ a typical relaxation time and } \langle F_f^2 \rangle_{\text{equ}} \text{ the mean-squared lateral surface force.}
\]

We then write \( \tau \sim \sigma^2/D \) where \( \sigma \) is a microscopic characteristic length scale and \( D \) the fluid diffusion coefficient, while the rms force is estimated as \( \langle F_f^2 \rangle_{\text{equ}} \sim C_\perp \rho \sigma^2(\varepsilon/\sigma)^2 \), with \( \varepsilon \) a typical fluid–solid molecular energy, \( \rho \) the fluid density and \( C_\perp \) a geometric factor that accounts for roughness effects at the atomic level (large \( C_\perp \) corresponding to a larger atomic roughness).\(^{25,63}\)

Altogether this provides a microscopic estimate for the slip length as

\[
b \sim \frac{k_B T \eta D}{C_\perp \rho \varepsilon^2} \tag{11}
\]

A more systematic derivation leads to a very similar result,\(^{21,62}\) with eqn (11) multiplied by the inverse of the structure factor of the fluid, \( S_n(q) \), computed at a characteristic wave-vector of the solid surface \( q_s \): \( b \propto S_n(q_s)^{-1} \). This term measures a kind of commensurability of the fluid with the underlying solid structure, in full analogy with solid-on-solid friction. Note also that the slip length depends on the product \( \eta \times D \), so that according to the Stokes–Einstein relationship, the slip length is not expected to depend on the bulk fluid viscosity (except for specific situations where these two quantities can be decorrelated). The scalings proposed by the above simple estimate are in good agreement with molecular dynamics results.\(^{21,63}\)

According to eqn (11) significant slippage should occur on very smooth surfaces, in the case of a low density at the wall (which requires both a moderate pressure and unfavorable liquid–solid interactions), or a low value of \( S_n(q_s) \), which characterizes liquid/solid commensurability. It also suggests that low energy surfaces, i.e. with small liquid–solid interaction \( \varepsilon \), should exhibit large slippage. Accordingly, hydrophobic surfaces should exhibit larger slip length than hydrophilic ones.

We plot in Fig. 4 (top) results for the slip length obtained by Molecular Dynamics of a water model over a broad variety of surfaces.\(^{45,63}\) A ‘quasi-universal’ dependence of the slip length on the contact angle is measured, with—as expected from the above arguments—an increase of the slip length for more hydrophobic surfaces.

**B Experimental results**

On the experimental side a race has engaged toward the quantitative characterization of BCs within nanometer resolution, using the most recent developments in optics and scanning probe techniques.\(^{55,56}\) This experimental challenge has generated considerable progress in experimental tools for nanofluidic measurements, and the values of the slip lengths reported had a tendency to decrease as the resolution and robustness of the techniques has increased. An intrinsic difficulty stems from the fact that the BC is a continuous medium concept involving an hydrodynamic velocity averaged on many molecules in the liquid and extrapolated to the wall: it does not simply reduce to the velocity close to the surface of molecules or tracer particles, which are furthermore submitted to Brownian motion and reversible adsorption. Also, the surface has to be smooth and homogeneous on the scale of the probed area in order to characterize an intrinsic BC, and not an effective slip length. Thus, the problem of the BC has been a discriminating test of the capacity of instruments to perform quantitative mechanical measurements at the nanoscale. We propose here a brief overview of the current state-of-the-art. This offers the opportunity to quote the various tools which have been developed recently to study flow and fluid dynamics at nanofluidic scales.
The Surface Force Apparatus provided the first sub-nanometer resolution measurement of BCs, based on the viscous force \( F_v \) acting between two crossed cylinders whose distance \( D \) is measured within Ångström resolution by the so-called FECO interferometric fringes.\(^{64}\)

\[
F_v = 6\pi \eta R^2 \frac{D}{b} f^* \tag{12}
\]

\[
f^* (D/b) = \frac{D}{3b} \left[ \left( 1 + \frac{D}{6b} \right) \ln \left( 1 + \frac{6b}{D} \right) - 1 \right] \tag{13}
\]

with \( \eta \) the liquid viscosity and \( R \) the cylinder radius.\(^{65}\) In case of a no-slip BC, \( F_v \) reduces to the Reynolds force between a sphere and a plane. Chan and Horn\(^{13}\) investigated the flow of various organic liquids confined between atomically flat mica surfaces and showed that they obeyed the no-slip BC, with the no-slip plane located about one molecular size inside the liquid phase. Their results were confirmed by other experiments running the SFA in a dynamic mode, and extended to water and to various (wetting) surfaces.\(^{14,66}\) Further investigations focused on non-wetting surfaces and reported the existence of very large slip lengths (\( \approx 1 \mu m \)) associated to a complex behaviour, with slippage appearing only under confinement and above a critical shear stress.\(^{67}\) However it was shown that elasto-hydrodynamics effects due to non perfectly rigid surfaces (such as glued mica thin films) retrieve this typical behaviour.\(^{68}\) Experiments on rigid surfaces later reported the existence of substantial slippage of water on smooth homogeneous non-wetting surfaces, with a slip length increasing with the contact angle and reaching a range of 20 nm at contact angles of 110 degrees.\(^{69,70}\) see Fig. 4.

The AFM with a colloidal probe operates along a similar principle but with a smaller probed area than the SFA. In pioneering investigations Craig et al.\(^{71}\) found a shear-rate dependent BC of sucrose solutions on partially wetting SAMs, with slip lengths reaching 20 nm at high velocities,\(^{71}\) while Bonacurso et al.\(^{72}\) found a constant (no shear dependent) slip length of 8–9 nm for water on wetting mica and glass surfaces.\(^{72}\) These dissimilar findings also did not agree with available theoretical results. However Ducker et al.,\(^{73}\) using an independent optical measurement of the probe-distance in the AFM, found a regular no-slip BC on a similar system as the one investigated by Craig et al.\(^{71}\) It was recently shown by Craig et al.\(^{74}\) that the lateral tilt of the cantilever was a significant issue in interpreting hydrodynamic forces.\(^{74}\) Vinogradova et al.\(^{75}\) also evidenced the important effect of the dissipation due to the cantilever.\(^{75}\) Using a “snow-man” probe made of two spheres glued on the top of each other, they showed a perfect agreement with the no-slip BC on hydrophilic surfaces, confirming SFA experiments, and a moderate slip length of 10 nm of water onto rough hydrophobic surfaces. Finally dynamic measurements using an oscillatory drive were implemented in the AFM by Maali et al.\(^{76}\) so as to measure the dissipation coefficient with high accuracy.\(^{76}\) Using this technique they found a no-slip BC of water onto mica surface, and a 8 nm slip length on atomically smooth highly ordered pyrolytic graphite (HOPG) with contact angle 70 degrees.\(^{77}\)

An alternative way to measure interfacial hydrodynamic dissipation is through the dissipation–fluctuation theorem, for instance by measuring the modification of the Brownian motion of a probe at the vicinity of a surface. In Joly et al.\(^{78}\) experiment\(^{72}\) the average transverse diffusion coefficient of colloidal particles confined in a liquid slab was measured by Fluorescence Correlation Spectroscopy as a function of the film thickness, and related to the boundary condition on the slab walls. A resolution better than 5 nm is obtained with particles of 200 nm nominal diameter, by averaging the data over 100 000 events crossing the measurement volume. The originality of the method is to give access to the boundary condition without any flow, \( i.e. \) really at thermodynamic equilibrium. It is thus directly comparable to theoretical predictions. A collateral result is the direct probe of a property of great interest in nanofluidics, \( i.e. \) the motion of a solute close to a wall.

Besides the dissipative methods, great progress was achieved in the development of optical methods giving direct access to the flow field and its extrapolation to the solid wall with a sub-micrometer resolution. The Micro-Particle Image Velocity (\( \mu \)-PIV) technique has been widely used in microfluidics. First attempts to determine the BC yielded slip lengths of micrometer amplitude,\(^{79}\) difficult to correlate with theoretical expectations, although the variation of slippage with the liquid–solid interaction were consistent. Gaining better resolution raised many issues. Besides colloidal forces acting on particles close to a wall, such as electro-osmosis induced by the streaming potential, which has to be taken into account, an important source of error is the depletion induced by the colloidal lift.\(^{79}\) By using the signal of non-moving particles adsorbed to the wall Joseph et al.\(^{80}\) increased the resolution on the slip length to 100 nm in a configuration similar to ref. 78, and found no slippage at this (100 nm) scale whatever the wettability of the surface. A recent investigation using double-focus FCS confirmed the existence of slippage of a few ten nanometers on hydrophobic surfaces.\(^{81}\) A major improvement toward nanometric resolution is the Total Internal Reflection Fluorescence method which uses an evanescent wave at the interface to be probed, and allows the measurement of the distance of a tracer particle to the wall through the exponential decay of the signal amplitude.\(^{82,83,84,103}\) Bouzigues et al.\(^{85}\) found a water slip length of 21 nm (\( \pm 12 \) nm) on OTS coated glass capillaries,\(^{103}\) while Lasne et al. measured a water slip length of 45 nm (\( \pm 15 \) nm) on a similar surface.\(^{84}\) These results are consistent and the different values of slip length may well be ascribed to slight variations in surface preparation. Note that in such measurements, the size of the probe itself is a major issue in the race toward nanometric resolution: Brownian motion increases as the particle size decreases, not only adding noise to the measurement, but allowing particles to leave the focal plane between two successive images which decreases the locality of the measurement. Some specific statistical treatment has to be performed in order to avoid any bias in the estimated velocity.\(^{84,85,103}\)

A summary of the results obtained with water on various smooth surfaces is gathered in Fig. 4 plotting the slip length as a function of the contact angle. The various methods show the same trend: water does not slip on hydrophilic
surfaces, and develops significant slippage only on strongly hydrophobic surfaces. The highest slip lengths reach the range of 20–30 nm; accordingly hydrodynamic slippage is non-relevant in microfluidic devices, but of major importance in nanochannels. On this basis one expects that water flow in highly confined hydrophobic pores, such as mesoporous media or biological channels (cf. the Aquaporin example in the Introduction), should be much less dissipative than ordinary Poiseuille flow. The results obtained with the various methods show a very good qualitative agreement with theory and molecular dynamics simulations performed with water. However the experimental slip lengths show a systematic bias toward higher values than theoretical ones. The discrepancy is actually not understood and might be the effect of gas adsorbed at the wall, possibly condensed in nanobubbles, an active research area recently.66,87,88

Finally, the case of organic molecules still raises debates. In the case of perfect wetting, various works on mica surfaces,13,18 as well as on glass surfaces,14,70 showed that alkanes and OMCTS have a no-slip velocity either at the wall or at a molecular size inside the liquid phase (negative slip length). However Pitt et al., using a fluorescence recovery method with molecular probes in a TIRF configuration, found very large slip lengths (∼100 nm) of hexadecane and squalane on atomically smooth saphir surfaces although these liquids wet perfectly the saphir.89,90 Further work is in progress to understand if these large slip lengths in the case of favorable solid–liquid interactions reflect a particular effect of molecular structure and incommensurability at the saphir/liquid interface.

More generally, although the problem of the boundary condition has generated an impressive instrumental progress in the quantitative measurement and control of flows at a nanoscale, a full quantitative confrontation with the theory, e.g. eqn (11), is still lacking.

IV. Nanometric diffuse layers and transport therein

The transport of electrolytes within the EDL and the associated phenomena have been extensively studied during the last century due in particular to its central role in colloid science. It has been accordingly discussed exhaustively in textbooks and reviews42,91 and in the present section we merely point to the main concepts which will be useful for our discussion.

In spite of this long history, new directions and perspectives have been opened very recently in this old domain. Novel insight into the nanometric Debye layer have indeed been reached: new tools now make it possible to investigate the detailed structure and dynamics inside the Debye layer. This concerns both the experimental side, see previous section, and numerical side, with the development of ever more powerful Molecular Dynamics tools.

From these more ‘molecular’ views of the EDL, in contrast to the more standard ‘continuum’ picture, new concepts and phenomena have emerged. We shall thus merely focus here on the recent progress and new leads opened by nanofluidics in this domain.

A From Debye layer to ion specific effects

An EDL builds up at a charged interface: it is the region of finite width where the surface charge is balanced by a diffuse cloud of counterions.91 The Debye layer is usually described on the basis of the mean-field Poisson–Boltzmann (PB) theory, see ref. 39 for a review. Ions are described as point charges and only their valency enters the description. Correlations between charges are accordingly neglected. The thermodynamic equilibrium balancing the ions entropy to their electrostatic interaction with the surface (attraction for the counter-ions and repulsion for the co-ions) leads to the introduction of the Debye length, as introduced above in eqn (5) and which we recall here:

$$\lambda_D = (8\pi \varepsilon \rho_p)_e^{-1/2}$$

Getting more into details, the PB description results from the combination of (i) the Poisson equation relating the electrostatic potential V to the charge density \( \rho_e = e(\rho_+ - \rho_-) \) according to

$$\Delta V = -\frac{\rho_e}{\varepsilon}$$

with \( \varepsilon \) the dielectric constant, here identified to its bulk value, and \( \Delta \) the spatial Laplacian; and (ii) the thermodynamic equilibrium leading to a spatially constant electro-chemical potential for the ions:

$$\mu_\pm = \mu(\rho_\pm) \pm Z_\pm eV$$

with \( Z_\pm \) the ion valency, \( \rho_\pm \) the ion densities and under the above assumptions, \( \mu(\rho) = \mu_0 + k_BT \log \rho \) the perfect gas expression for the chemical potential.

Though its crude underlying assumptions, the mean-field PB theory captures most of the physics associated with the EDL and is the usual basis to interpret ion transport. One reason for this success is that ion correlations within the EDL, which are discarded in PB, can generally be neglected. This can be quantified by introducing a coupling parameter, \( \Gamma_{cc} \), which compares the typical inter-ions electrostatic interaction to thermal energy.92,93 Following ref. 92 and 93, the latter is estimated as \( \Gamma_{cc} \approx e^2/(4\pi\varepsilon\rho k_BT) = l/l_p \), with \( l \) the mean distance between ions at the surface. This scale is related to the charge density \( \Sigma \), as \( \Sigma \approx l^{-1/2} \), so that \( \Gamma_{cc} \approx \sqrt{\Sigma^2} \).34 PB is expected to break down when the coupling parameter exceeds unity. For typical surfaces this threshold is not reached: for glass, the surface charge is at most in the 10^{-2} C/m^2 range (∼6 × 10^{-2} e/nm^2), and the coupling parameter \( \Gamma_{cc} \) remains smaller than unity.

Other assumptions inherent to PB could be also questioned. In the PB description, the dielectric constant is assumed to be spatially uniform and identical to its bulk value. This assumption is expected to break down very close to surfaces, in particular hydrophobic, where water ordering induces a local electric dipole pointing outward to the interface.94 This casts some doubts on the local relation between medium polarization and local electric field. However MD simulations suggest that using the bulk dielectric constant in the Poisson equation is not a critical assumption and can be safely used to describe the EDL.94
PB description however misses an important class of effects associated with the specific nature of ions, and which affect the fine structure of the EDL. Ion specificity is intimately connected to Hoffmeister effects, namely that the interactions between charged and neutral objects in aqueous media do depend crucially on the type of ion and not only on electrolyte concentration.\textsuperscript{95–97} Such effects occur not only at the air–water interface, where it does affect surface tension depending on ion type, but also at hydrophobic surfaces.\textsuperscript{96,98} This effect is evidenced in Fig. 5, where results of molecular dynamics simulations of ions dispersed in water (SPC-E model) from ref. 98 demonstrate that iodide ions do strongly adsorb at air–water and hydrophobic interfaces, while chloride ions do not. Note that an EDL builds up even in the case of a neutral interface, we shall come back to this result and its implications. In general heavier halide ions adsorb at the neutral interface, we shall come back to this result and its implications. In general heavier halide ions adsorb at the neutral hydrophilic surfaces. From ref. 98.

Let us first discuss electro-osmosis (EO). EO is the phenomenon by which liquid flow is induced by an electric field. In its simplest form, the fluid velocity $v_f$ beyond the EDL is linearly connected to the applied electric field $E_e$ according to the Smoluchowski formula:\textsuperscript{42}

$$v_f = -\frac{\varepsilon e}{\eta} E_e$$

(17)

with $\varepsilon$ the dielectric constant, $\eta$ the viscosity and $\zeta$ the so-called zeta (electrostatic) potential. The common interpretation of $\zeta$ is that it is the electrostatic potential at the “shear plane”, i.e. the position close to the wall where the hydrodynamic velocity vanishes. As we now discuss, this interpretation should be taken with caution.

Let us briefly recall the derivation of eqn (17). Fluid dynamics is described by the stationary Stokes equation:

$$\frac{\partial^2 v_f}{\partial z^2} + \rho_f E_e = 0$$

(18)

Here we use a frame where the electric field $E_e$ is along $x$ and parallel to the planar surface, and the velocity field $v_f$ only depends on the direction $z$ perpendicular to it.

A key remark, already mentioned above, is that the charge density, $\rho_f = e(\rho^+ - \rho^-)$, is non-vanishing only within the EDL, so that the driving force for fluid motion, $F = \rho_f E_e$ is limited to that nanometric region, and vanishes otherwise. In order to obtain the velocity profile, the Stokes equation should be integrated twice, and thus requires two boundary conditions. Far from the surface, the velocity profile is plug-like and $\partial_z v|_{z=\infty} = 0$. At the wall surface, the hydrodynamic boundary conditions for the hydrodynamic velocity profile should be specified. We have discussed above that the latter introduces a slip length $b$, according to eqn (7), as $b\delta v|_{z=0} = v(z = 0)$. Using Stokes and Poisson equations, one sees immediately that the full velocity profile is related to the electrostatic potential $V$ as

$$v(z) = -\frac{\varepsilon e}{\eta} E \times [\nabla V(z) + \zeta]$$

(19)

where $\zeta$ has the meaning of a zeta potential\textsuperscript{156} and takes the expression

$$\zeta = V_0 \times (1 + b \kappa_{\text{eff}})$$

(20)

where $V_0$ is the electrostatic potential at the wall and $\kappa_{\text{eff}}$ is the surface screening parameter, defined as $\kappa_{\text{eff}} = -V(0)/V_0$.\textsuperscript{94,100} For weak potentials this reduces to the inverse Debye length: $\kappa_{\text{eff}} \approx \lambda \rho^+ \varepsilon$, but its full expression takes into account possible non-linear effects. The fluid velocity far from the surface (i.e. outside the EDL) has the Smoluchowski expression above, eqn (17), with the expression of the zeta potential, $\zeta$, given in eqn (20). This prediction was first discussed in ref. 101, and rederived independently in more recent works.\textsuperscript{94,100} We emphasize that the above result, eqn (19)–(20), does not make any assumption on the specific model for the EDL, except for a uniform dielectric constant $\varepsilon$ and the validity of the Stokes equation, which was discussed above to be valid down to the nanometer scale.

The physical meaning of the above expressions is quite clear. The velocity in the fluid results from a balance between the

**Fig. 5** Simulated density profiles of negative ions (solid lines), positive ions (dashed lines) and water (dotted lines) for roughly 1 M solutions of (a) NaI and (b) NaCl between neutral hydrophobic surfaces, (c) NaI at a vapor–liquid interface and (d) NaI between neutral hydrophilic surfaces. From ref. 98.
driving electric force and the viscous friction force on the surface. Per unit surface, this balance writes
\[ \eta \frac{v_{\infty}}{\lambda_D + b} \approx eS \times E \] (21)

with \( \Sigma \) the surface charge density (in units of \( \text{m}^{-2} \)) at the wall. The expression for the viscous friction expresses the fact that flow gradients occur on a length \( b + \lambda_D \), see Fig. 6. Relating the surface charge to the surface potential \( V_0 \) \((e\Sigma = -e\partial_z V_0)\), one recovers the above results.

As a side remark, one may note that the slip enhancement does not require any assumption on the electric and fluid behavior. Indeed at a fully general level, the (exact) momentum balance at the surface shows that the velocity at the wall is exactly given by \( v_{\text{wall}} = \frac{b}{\lambda_D} E \), with \( D_{\text{wall}} \) the dielectric displacement computed at the surface, and \( \lambda \) the surface friction coefficient introduced in eqn (9). The latter is related to the slip length according to the definition \( \lambda \equiv \eta/b \). This expression for the wall velocity under an applied electric field neither invokes Navier–Stokes equation, nor any assumption on the dielectric behavior. This wall velocity acts as a lower bound to the asymptotic EO velocity, i.e. the one measured at infinite distance from the surface. This demonstrates that the enhancement of the EO velocity due to low liquid–solid friction, i.e. large slippage, has a fully general validity.

Several conclusions emerge from eqn (20). First, if the wall is characterized by a no-slip BC, with \( b = 0 \), then the zeta potential \( \zeta \) identifies with the electrostatic potential \( V_0 \) computed at the surface (up to a possible molecular shift due to the precise position of the hydrodynamic BC which defines the so-called shear plane [100]); this is the common assumption, as usually expressed in textbooks.\(^42\) Now, if finite slippage occurs at the surface, then the zeta potential is much larger than the surface electrostatic potential, \( V_0 \); it is amplified by a factor \( 1 + b/\lambda_D \) (assuming for the discussion that \( \kappa_{\text{eff}} = \lambda_D^{-1} \)). This factor may be very large, since on bare hydrophobic surfaces \( b \) may reach a few tens of nanometers (say \( b \approx 20–30 \) nm), while the Debye length typically ranges between 30 nm down to 0.3 nm (for \( 10^{-4} \) M to 1 M).

These predictions have been confirmed by molecular Dynamics simulations of electro-osmosis (and streaming current, see below).\(^34,98,100\) Various systems were considered, from a model electrolyte involving ions in a Lennard-Jones solvent, to a more sophisticated SPC-E model of water, with ions of various nature. Altogether simulations confirm the key role of slippage on electrokinetics and results do fully agree with the above description.

On the experimental side, this strong influence of surface dynamics on the electrokinetics at surfaces has not been appreciated and explored in the electrokinetic literature up to now, and very few experimental investigations have been performed on this question.\(^102,103\) One key difficulty is that the above result for the zeta potential, eqn (20), involves a strong entanglement between electrostatics, through surface potential, and fluid dynamics, through hydrodynamic slippage. In order to disentangle the two effects, two independent measurements of these quantities should in principle be performed. To our knowledge the first work on the subject was performed by Churaev et al. in ref. 102, and results indeed suggested a slip effect, at the expense however of a rather uncontrolled assumption on the surface potential. More recently this problem was tackled in ref. 103 using the nanoPIV tool discussed above. This set-up allows for two independent measurements of \( \zeta \) and \( V_0 \), leading to an unambiguous confirmation of the above predictions of slippage effect on the zeta potential. Indeed both the velocity profile, which is fitted to eqn (19), and the nanocolloid concentration profile, from which the surface potential is deduced on the basis of the electrostatic repulsion, are measured independently. Velocity profiles from ref. 103 are displayed in Fig. 7. While the two surfaces under consideration (a hydrophilic glass and a silanized hydrophobic surface) had basically the same surface potential, a factor of two is found on the zeta potential under the conditions of the experiment. Results are consistent with a slip length of \( \approx 40 \) nm. The factor of two for \( \zeta/V_0 \) occurs here due to a Debye length of \( \approx 50 \) nm in the experimental condition of ref. 103 (a large Debye length is required to investigate flow inside the Debye layer at the present spatial resolution, \( \approx 20 \) nm, of the nanoPIV technique). As a side remark, note the large slip velocity at the wall in the slippy case in Fig. 7: this is expected since according to eqn (19), the velocity at the surface is directly proportional to the slip length \( b \), as \( v(0) = -\zeta E / V_0 e \text{eff} \) (assuming, to simplify, that \( \kappa_{\text{eff}} \approx \lambda_D^{-1} \)).

This result opens up a new perspective to make use of surface physico-chemistry in order to optimize electric-induced transport and control flow by surface properties. It was also argued that such slip-induced optimization would strongly enhance the efficiency of energy conversion devices based on electrokinetic effects.\(^104,105\)

Besides slip effect, ion-specificity also has an important influence on the electro-osmotic transport. As we reported above, the structure of the EDL is affected by the nature of the ions under consideration, especially at hydrophobic walls (air–water interfaces). This can be best seen by rewriting the expression for the zeta potential, in eqn (20), in a slightly different form:
\[ \zeta = -\frac{1}{e} \int_0^\infty (z' + b) \rho_c(z') \; dz' \] (22)
with \( \rho_c \) the charge density. This expression e.g. comes from the double integration of the Stokes law. As seen in Fig. 5 ion specific effects have a strong influence on the charge distribution, and do indeed strongly modify the value of \( \zeta \). This effect was
Electrostatic potentials were independently measured to be comparable inside the EDL. According to the Onsager symmetry application of a pressure gradient, again, since the EDL is not a phenomenon, by which an electric current is induced by the electro-osmotic transport also applies to the streaming current potential. For analytical predictions for ion-specific effects on the zeta potential, the solvation free-energy of ions close to the interface allows (top) and 

\[
\frac{z}{C_0} = \frac{1.5}{C_{\text{D}}}
\]

larger solvation energy and are therefore attracted to hydrophilic (pyrex) surface and \( V_0 \approx -65 \text{ mV} \) for the hydrophilic (OTS-coated) surface. The salt concentration is \( 1.5 \times 10^{-4} \text{ mol L}^{-1} \) and the driving electric field is \( E = 500 \text{ V m}^{-1} \). Dashed lines are fits to the theoretical predictions using eqn (19), with \( \lambda_0 = 51 \pm 10 \text{ nm} \) (measured independently) and \( b = 0 \pm 10 \text{ nm} \) (bottom) and \( b = 38 \pm 6 \text{ nm} \) (top) for the slip lengths. Figure from ref. 103.

More quantitatively, effects of ion-specificity on the zeta potential were rationalized in ref. 94 on the basis of a minimal model, which was subsequently validated on MD simulations. This description is based on the idea that ‘big’ ions have a larger solvation energy and are therefore attracted to hydrophobic interfaces in order to minimize this cost. An estimate of the solvation free-energy of ions close to the interface allows for analytical predictions for ion-specific effects on the zeta potential.

We finally quote that all of the above discussion on the electro-osmotic transport also applies to the streaming current phenomenon, by which an electric current is induced by the application of a pressure gradient. Again, since the EDL is not electro-neutral, liquid flow will induce an electric current inside the EDL. According to the Onsager symmetry principle, these two phenomena—electro-osmosis and streaming current—are intimately related and the cross coefficients should be identical. The expression for the streaming current \( I_s \) under an applied pressure gradient \( \nabla P \) takes the form:

\[
I_s = -\frac{z}{\eta} \phi \langle -\nabla P \rangle
\]

where \( z \) takes the same expression as in eqn (20) and \( \phi \) is the cross sectional area of the channel.

We end this section by mentioning that the above effects generalize to any interfacial transport phenomena. Indeed the above electrically induced phenomena belong to a more general class of surface induced transport, which also involves phenomena known as diffusio-osmosis or thermo-osmosis and their associated phoretic phenomena for colloidal transport. Thermooosmosis points to fluid motion induced by thermal gradients, while diffusio-osmosis corresponds to fluid flow induced by gradients in a solute concentration. Though relatively old, thermophoretic transport has been the object of recent investigations in particular for colloidal manipulation. Its origin is still the object of an intense debate with recent progress in disentangling the various contributions. On the other hand, diffusiophoretic and osmotic transport have been less explored but their potential in the context of microfluidic applications has been demonstrated recently. This opens up the novel possibility of driving and pumping fluids as well as manipulating colloids— with solute contrasts, which have been barely explored up to now and would deserve further investigations in the context of nanofluidics. A common point to all these phenomena is their “nanofluidic root”: as for the electro-osmotic transport discussed above, the driving force for fluid motion is localized within a diffuse layer of nanometric size close to the surfaces. Therefore, this opens up the possibility of strongly amplifying their effect on the basis of slippage effects at the solid interface. As demonstrated theoretically in ref. 115, the amplification is—as for electro-osmosis above—amplified by a factor \( 1 + b/\lambda \), where \( \lambda \) is the width of the diffuse layer. Similar effects are predicted for thermophoretic transport.

Finally, one may raise the question of interfacial transport on super-hydrophobic surfaces. Such surfaces, achieved using nano- or micro-engineering of the surfaces, were shown to considerably enhance the slippage effect and exhibit very large slip length in the micron (or even larger) range. Accordingly, a naive application of the previous ideas would suggest massive amplification by a factor up to \( 10^9 \). However, the composite structure of the superhydrophobic interface, involving both solid–gas and liquid–gas interfaces, makes these transport mechanisms far more complex in this case than on a smooth interface. It has been shown that in the regime of a thin Debye layer, no amplification is obtained for electro-osmosis on superhydrophobic surfaces, unless a non-vanishing charge exists at the liquid–gas interface. In contrast, a massive amplification is predicted for diffusio-osmosis. This strong prediction has not received an experimental confirmation up to now.

C Surface versus bulk: conductance effects

We now discuss the surface conductance effect in nanochannels. The conductance, \( K \), characterizes by definition the electric current versus electric potential drop relationship. As pointed out previously, conductance probes the number of free charge carriers, here ions. In the bulk \( K \) is therefore expected to be proportional to the salt concentration \( \rho_s \) (ionic strength). Now in the presence of surfaces, the charges brought by the surface lead to a supplementary contribution to the conductance.
Surface conductance is actually a rather classical phenomenon in colloid science, \(^\text{42}\) but it was demonstrated quite recently in the context of nanochannel transport by Stein et al.\(^\text{44}\) and then by other groups.\(^\text{44}\)

As we introduced in section II B 2.c, the ratio of bulk to surface charge carriers is characterized by the Dukhin length \(\ell_{Du}\). This length accordingly describes the competition between bulk and surface conductance. Depending on salt concentration, this length can be much larger than the Debye length. Surface conductance is therefore expected to dominate over the bulk contribution for nanochannels smaller than \(\ell_{Du}\). The magnitude of the surface conductance effect is amplified in small channels, but a key point is that it does not require Debye layer overlap.

Experimentally, the surface contribution to the conductance shows up as a saturation of the conductance in the limit of small salt concentration, while its expected bulk counterpart is expected to vanish in this limit. The saturation originates in the charge carriers brought by the surface charge, the number of which is independent of the salt concentration. This is illustrated in Fig. 8, from ref. 41, where the conductance is measured in channels of various width, from 1015 nm down to 70 nm.

Let us discuss more specifically this point. In a slit geometry with width \(h\), the general expression for the current (for a unit depth of the slit) takes the form

\[
I_c = e \int_{-h/2}^{h/2} dz [\rho_+(z) \nu_+(z) - \rho_-(z) \nu_-(z)]
\]

where the averaged velocities of the ions is

\[
\nu_{\pm}(z) = \nu(z) \pm e \mu_{\pm} E_w
\]

with \(\mu_\pm\) the ion mobility, defined here as the inverse of the ion friction coefficient (we assume furthermore \(\mu_\pm = \mu\)). The velocity \(\nu(z)\) is the fluid velocity induced by electro-osmosis under the electric field, as given in eqn (19). The second term is the contribution to the current due to ion electrophoresis.

Combining the expression of the velocity \(\nu(z)\), as in eqn (19), to eqn (24)-(25), one may remark that the electro-osmotic contribution to the current takes the form of the integral of the charge density times the electrostatic potential: this has therefore the form of an electro-static energy, \(\delta\). This is confirmed by the full calculation, which leads to a conductance expression in the form: \(^\text{41,118}\)

\[
I/E_w = 2e^2 \mu_{\pm} \delta (1 + H)
\]

with \(\delta\) the channel cross section (\(\delta = w \times h\) with \(w\) the depth of the channel) and the surface correction \(H\)

\[
H = \cosh \left( \frac{e V_c}{k_B T} \right) - 1 + \frac{\delta}{4 \rho \nu \theta} \left( 1 + \frac{1}{2 \pi \ell_{Du} \mu} \right)
\]

where \(V_c = V(0)\) is the electrostatic potential at the center of the channel, and \(\delta = \frac{1}{2} \int_0^h dz (\frac{\partial \Phi}{\partial \nu})^2\) the electrostatic energy (and not the free energy). Note that writing \(\mu = 3 \pi n_d \eta\) with \(d_i\) the ion diameter, the last term in eqn (27) is typically of the order \(d_i/\ell_B\). It originates in the surface-induced—electro-osmotic—contribution to the conductance.

In the low salt concentration regime, \(\rho_+ \rightarrow 0\), the length scales are organized in the order:

\[
\ell_{GC} < \lambda_D < \ell_{Du}
\]

since \(\lambda_D/\ell_{GC} = \ell_{Du}/\lambda_D \gg 1\) for \(\rho_+ \rightarrow 0\). Saturation will occur as the channel width \(h\) is smaller than the Dukhin length, \(h < \ell_{Du}\) independently of the order of \(h\) and \(\lambda_D\). Debye layer overlap is accordingly not the source of the saturation of the conductance. In this regime, the second term in eqn (27), associated with surface contributions is dominant.

In this limit, the calculation of the electrostatic energy shows that \(\delta \sim |\Sigma|\). The fact that \(\delta\) scales linearly in \(|\Sigma|\) and not as \(|\Sigma|^2\)—as would be first guessed—is due to the non-linear contributions to \(\delta\) in the Poisson-Boltzmann description. These become dominant in the \(\rho_+ \rightarrow 0\) limit where the Debye length becomes larger than the Gouy-Chapman length. Altogether, this shows that for \(\rho_+ \rightarrow 0\), the conductance saturates at a value

\[
K_{sat} \approx e^2 [w \times 2|\Sigma| \left( 1 + \frac{1}{2 \pi \ell_{Du} \mu} \right)]
\]

with \(w\) the depth of the channel. This value is independent of both \(h\) and \(\rho_+\). This saturation can be also partly understood in the context of Donnan equilibrium discussed below. In the limit \(\rho_+ \rightarrow 0\), only the counter-ion contributes to the ion concentration in the channel, \(\rho_+ + \rho_- \approx 2 \Sigma/h\), see eqn (34) below, so that the conductance reduces to \(K_{sat} \approx e^2 [w / 2|\Sigma|]\). This analysis however misses the electro-osmotic contribution to the conductance (second term in the brackets in eqn (29)).

A few remarks are in order. First, the dependence of the conductance on the surface properties, here the surface charge \(\Sigma\), opens new strategies to tune the nanochannel transport properties, via an external control. This has been used by Karnik et al. to develop a nanofluidic transistor,\(^\text{5}\) allowing the control of the conductance of the nanochannel thanks to a gate voltage.

![Fig. 8](image-url) Channel height dependence of ionic conductance behavior. The conductance of fluidic channels is plotted against salt concentration for various nanochannel width \(h\) (\(h = 1015, 590, 380, 180\) and 70 nm). The inset displays the fit values for the surface charge at the nanochannel walls as a function of \(h\). From ref. 41.
Another interesting remark is that along the same line as in section IV B, the electro-osmotic contribution to the conductance could be also amplified by slippage effects. This can be readily demonstrated by a direct integration of eqn (24). Accordingly slippage effects add a new contribution to the conductance:

$$K_{\text{slip}} = 2e^2 w z^2 \eta / b$$

Assuming Stokes law for ion inverse mobility ($\mu = (3\pi \eta d_{\text{ion}})^{-1}$ with $d_{\text{ion}}$ the ion size), then $K_{\text{slip}}/K_{\text{ion}} \sim b \times d_{\text{ion}} (\Sigma) \approx b / \lambda_{GC}$: since the Gouy–Chapman length $\lambda_{GC}$ is typically nanometric (or less), this enhancement is therefore very large, even for moderate slip length ($b \sim 30$ nm)!

The channel resistance is accordingly decreased by the same factor in the low salt regime. This amplification of conductance by hydrodynamic slippage opens very interesting perspectives in the context of electrokinetic energy conversion, as was pointed out recently by Pennathur et al. and Ren and Stein. Moderate slippage, with slip length of a few tens of nanometers, is predicted to increase the efficiency of the energy conversion up to 40% (and of course even more with larger slip lengths). This attracting result would deserve a thorough experimental confirmation.

D  Debye layer overlap and nanofluidic transport

The phenomenon of Debye layer overlap has already been widely explored in the nanofluidic literature. As we pointed out above, various reasons underlie this specific interest: (i) well controlled nanometric pores with size in the range 20–100 nm can be produced using micro-lithography techniques; this does indeed correspond precisely to the range of typical Debye lengths for usual salt concentrations (remember that $\lambda_D = 30$ nm for a salt concentration of $10^{-4}$ M); (ii) the overlap of Debye length does indeed have a strong influence on ion transport, so that novel transport effects emerge at this scale, with applications for chemical analysis.

The question of Debye layer overlap, and related phenomena, was discussed quite extensively in a recent review by Schoch et al. Here we thus focus on the main guiding lines underlying this problem and point to the key physical phenomena at play. In particular we shall discuss an illuminating analogy to transport in semi-conductors.

1. Donnan equilibrium. An important notion underlying the Debye overlap is the so-called “Donnan equilibrium”, which is a well known concept in colloid literature. Due to the supplementary charges brought by the nanochannel’s surface, a potential drop builds up between the nanochannel’s interior and the external reservoir, in order to maintain a spatially uniform chemical potential of the ions. The latter, as introduced above, takes the form (assuming a dilute ion system):

$$\mu(\rho_{\pm}) = \mu_0 + k_B T \log(\rho_{\pm}) \pm e V = \mu_0 + k_B T \log(\rho_s)$$

with $\rho_s$ the (uniform) salt concentration outside the nanochannel, i.e. the “reservoir”. These equations are completed with the overall electroneutrality over the channel,

$$\int_{b/h}^{L} dz (\rho_+(z) - \rho_-(z)) = 2 \Sigma$$

Fig. 9 (a) Sketch of the electrostatic potential in a charged slit with thickness $h$: (left) $h > 2\lambda_D$, and (right), $h < 2\lambda_D$, corresponding to Debye layer overlap. (b) A charged nanochannel, with thickness $h$ and length $L$, connects two reservoirs $R_1$ and $R_2$. In the situation of Debye layer overlap, a Donnan potential $V_D$ builds up along the nanochannel.

with $z$ along the direction perpendicular to the nanochannel (here assumed to be a slit), see Fig. 9.

We now focus on the thin pore limit, assuming Debye layer overlap $h \leq 2\lambda_D$. In this situation, ion densities and electrostatic potential are approximately spatially uniform over the pore thickness $h$. Ion densities thus obey:

$$\rho_+ - \rho_- = \rho_s^2$$

$$\rho_+ \times \rho_- = \rho_s^2$$

Altogether, this leads to

$$V_D = \frac{k_B T}{2e} \log \left( \frac{\rho_+}{\rho_-} \right)$$

where the mean electrostatic potential $V_D$ is denoted as the Donnan potential.

Note that the amplitude of the Donnan potential $V_D$ is quantified by the ratio $\lambda_{D_0} / h$ where $\lambda_{D_0} = \Sigma / \rho_s$ is the Dukhin length introduced above. To give an order of magnitude $\lambda_{D_0} \sim 1$ nm for $\rho_s = 1$ M and a typical surface charge.

It is finally of interest to mention the strong analogy between the Donnan equilibrium and the equilibrium of charge carriers in doped semi-conductors (SC). In the latter the electron density $\rho_e$ and the hole density $\rho_h$ obey eqn (33) with the electrolyte density $\rho_s$ replaced by the carrier density in the intrinsic (non-doped) SC. The surface charge in the nano-channel actually acts as impurities delivering additional carriers, with $\Sigma > 0$ corresponding to donors (N-doped SC) and $\Sigma < 0$ acceptors (P-doped SC). The Donnan potential is then the analogous of the shift in the Fermi energy due to impurities, which determines the voltage difference at equilibrium between regions of different doping level. The table hereafter, Table 1, summarizes the corresponding quantities in the nano-channel and SC analogy.
The Donnan potential and Debye layer overlap have many implications on nanofluidic transport.

2. Ion transport and PNP equations. A classical framework to discuss ion transport in narrow pores is the so-called Poisson-Nernst-Planck (PNP) equations. This simplified description of ion transport in strongly confined channels is based on the coupled diffusion-electro-convection of the ions.\textsuperscript{119}

As in Fig. 9, the channel thickness is assumed to be small compared to the Debye length, $h \ll \lambda_R$, so that ion concentrations are assumed to be uniform across its thickness. The ion fluxes $J_\pm$ (per unit surface) then takes the form

\[
J_\pm = -D_\pm \nabla \rho_\pm(x) \pm \mu_\pm e \phi_\pm(x) \nabla \phi(x) \tag{35}
\]

where $D_\pm$ and $\mu_\pm$ are related by the Einstein relationship, $D_\pm = \mu_\pm k_B T$; $x$ is along the direction of the channel. Note that for simplicity, a single salt and monovalent ions are considered here. A local version of the electroneutrality, eqn (33), may be made along the pore:

\[
\rho_+ - \rho_- = \frac{\Sigma(x)}{h} \tag{36}
\]

Finally at the pore entrance and exit, a Donnan electric potential drop builds up, along the description given above, see eqn (34).

To illustrate further this approach, we consider the transport through a single nanochannel, as sketched in Fig. 9(b). At equilibrium the two reservoirs, $R_1$ and $R_2$, have the same electric potential and salt concentration, associated with a uniform Donnan potential along the channel. Now if an electrostatic potential drop $\Delta V$ or a salt concentration difference $\Delta \rho_\pm$ is imposed between the reservoirs, ion fluxes will build-up so as to relax towards equilibrium.

In the stationary state, the ion flux is spatially uniform, so that one may solve eqn (35)-(36) for the ion densities and electrostatic potential. This allows the current $I = \mathcal{A} (J_+ - J_-)$ and total ion flux $\Phi_i = \mathcal{A} (J_+ + J_-)$ to be computed, with $\mathcal{A}$ the cross sectional area of the channel and $\Delta[\log \rho_i] = \Delta \rho_i / \rho_i$. Note that due to Onsager (time reversal) symmetry, the non-diagonal coefficients of the matrix are equal.\textsuperscript{121,122}

The coefficients of the above matrix can be calculated within the PNP framework. PNP equations are solved analytically for small potential and concentration drops, leading to the following expression for the various coefficients in the matrix, eqn (37):

\[
K = 2 \mu_e^2 \sqrt{\rho_e^2 + \left( \frac{\Sigma}{h} \right)^2}
\]

\[
\mu_{\text{eff}} = 2 \mu \times \sqrt{\rho_e^2 + \left( \frac{\Sigma}{h} \right)^2}
\]

\[
\mu_K = e \mu \times \frac{2 \Sigma}{h}
\]

We assumed here that ions have the same mobilities $\mu_\pm = \mu$. The cross effects, associated with the mobility $\mu_K$, originate in the dependence of the Donnan potential on the salt concentration.

Let us conclude this part with a few remarks:

- First one should realize that a number of assumptions are implicitly made in writing PNP equations. In particular the ions are treated as a perfect gas and correlations between ions along the channel are neglected. This may become problematic in strongly confined situations where single file transport (of the solvent) and strong unidirectional electrostatic correlations should build up. As an example, proton transport in single file water has been shown to involve a highly-cooperative mechanism.\textsuperscript{120} However these limitations are restricted to single file transport in molecular channels, and should not be a limitation for pore size larger than a nanometer. Furthermore the PNP model is interesting to explore as a guiding line, in the sense that it provides a rather correct physical idea of the (complex) electro-diffusion couplings.

- Furthermore, we may pursue the analogy discussed above between nanochannels and doped SC (see Table 1), and extend the discussion to transport phenomena. Indeed the Poisson–Nernst–Planck equations, eqn (35), are formally identical to the phenomenological transport equations for electrons and holes in SC. Thus, as long as electrical and concentration fluxes only are allowed, nanofluidic devices can in principle reproduce standard SC-based components, such as diodes and transistors. The nanofluidic diode for instance is based on the properties of a PN junction, i.e. the junction between two regions with different doping: according to the equivalence table, Table 1, its nanofluidic equivalent corresponds to two nanochannels with different surface charge $\Sigma/h$. We will discuss below (sub-section 5) some recent findings confirming the pertinence of this analogy.

- However one should keep in mind that the transport analogy between fluids and electrons breaks down in the presence of hydrodynamic flow. Actually, PNP equations introduced above do not take into account convective contributions. In a fluidic system, a flow is indeed expected to occur in nanochannels as soon as a voltage drop is applied to its end, due to the body force acting on the mobile charges, but also under a pressure gradient (hydrostatic or osmotic).

### Table 1 Equivalence table for corresponding quantities in doped semiconductors and nano-channels

<table>
<thead>
<tr>
<th>Nano-fluidics</th>
<th>Semi-conductors</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_-$ negative ions</td>
<td>$\rho_e$ electron density in the conduction band</td>
</tr>
<tr>
<td>$\rho_+$ positive ions</td>
<td>$\rho_h$ holes density in the conduction band</td>
</tr>
<tr>
<td>$\rho_i$ electrolyte concentration</td>
<td>$n_i$ carriers density in the intrinsic SC</td>
</tr>
<tr>
<td>Surface charge $2\Sigma/\hbar$</td>
<td>Impurities (doping) concentration</td>
</tr>
<tr>
<td>Donnan potential</td>
<td>Shift of the Fermi level</td>
</tr>
</tbody>
</table>

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This is for example the source of electro-osmotic or streaming current contributions discussed above. In contrast, SCs can not flow—quite obviously—under an applied electric field and may only deform elastically. This is therefore a limitation to the above analogy.

In the case of a strongly confined regime with a large slippage at wall, the hydrodynamical contribution to the ion flux could well become dominant. Such a convection contribution should therefore be added in the form \( J_{\text{conv}} = v_f \times \rho \), where \( v_f \) is the water velocity. The water velocity is in turn coupled to (electric) body forces via the momentum conservation equations, in practice the Navier–Stokes equation in its domain of validity. Altogether, the hydrodynamically induced cross phenomena, i.e. electro-osmosis, streaming currents, diffusio-osmosis, . . . (as well as bare osmosis), can be summarized at the linear level in terms of a symmetric transport matrix, in a form similar to eqn (37). This matrix relates linearly the fluxes to thermodynamic forces at work. These phenomena have been discussed extensively in the context of membrane transport but generalize here to transport in nanofluidic channels.

More generally the coupling of the ion transport to the fluid transport thus opens the route to new applications in nanofluidic devices, with a richer phenomenology than in SC electronics.

We now illustrate the above concepts in a few practical situations.

3. Permselectivity. As a first example, we consider the permeability of nanopore to ions. It was first shown by Plecis et al.2 that nanochannels exhibit a selective permeability for ion diffusive transport, see Fig. 10(a): ions of the same charge as the nanochannel surface (co-ions) exhibit a lower permeability, while ions of the opposite charge (counter-ions) have a higher permeability through the nanochannel.

This charge specific transport is a direct consequence of a non-vanishing Donnan potential in the nanochannel (and Debye layer overlap). As pointed out above, Fig. 9, counter ions exhibit a higher concentration in the nanochannel as compared to that of a neutral species, \( \rho_+ > \rho_0 \), while co-ions have correspondingly a lower concentration, \( \rho_- < \rho_0 \).

The diffusive flux of counter-ion will be accordingly larger than its expectation for neutral species, and vice versa for co-ions. This leads therefore to a charge-specific effective diffusion coefficient \( D_{\text{eff}} \) for the co- and counter-ions.

Following Plecis et al.2 the effective diffusion coefficient is defined according to the identity

\[
J_a = -D \frac{\Delta \rho_a}{L} \equiv -D_{\text{eff}} \frac{\Delta \rho_a}{L}
\]

(39)

taking into account the fact that the local concentration in the nanochannel differs from the one imposed at the two ends of the reservoir. The linearized Poisson–Boltzmann equation is then used to calculate the ion concentration in the slit, \( \rho_a \), as:

\[
\beta_a = \frac{\bar{\rho}_a(x)}{\bar{\rho}(x)} = \frac{1}{B} \int_{\text{slit}} dz \exp[\mp eV(z)/k_B T]
\]

(40)

\[
D_{\text{eff}}/D = \beta_a
\]

where, as shown in eqn (34), \( \beta_a = \sqrt{\rho_a^2 + \left(\frac{q}{k_B T}\right)^2} \). This expression reproduces the results in Fig. 10.

Finally, one should note however that due to the difference in ion permeability, a charge separation will build up between the two ends of the channel. This leads therefore to the creation of a reacting electric field along the channel, which will compensate dynamically for this charge separation.2 This points to the complex couplings associated with charge transport in nanochannels. More experimental and theoretical

---

**Fig. 10** Top Variation of the relative permeability of various probes with different charges, versus ionic strength. The experimental results are compared to theoretical fittings obtained with eqn (40) (dotted lines). Bottom Concentration profiles of counter- and co-ions, \( \rho_\pm \), for a given salt concentration drop \( \Delta \rho \) between the two ends of the nanochannel. The dotted line represents the linear concentration profile for noninteracting diffusing species, whereas plain lines show the ion profiles in the nanochannel. Adapted from ref. 2.
work is certainly in order to get further insight in these phenomena.

4. Pre-concentration. Along the same lines, another consequence of Debye layer overlap is the ‘pre-concentration’ phenomenon, which was first observed by Pu et al.,3 and others.125 Instead of a concentration drop as above, a voltage drop is applied along the nanochannel. It is then observed that ions enrich at one end and deplete at the other end. This phenomenon is illustrated in Fig. 11.

As above, a key point underlying the phenomenon is that ions of the opposite sign to the channel’s surface, counter-ions, are more heavily transported than co-ions. This will create an enriched/depleted zone for both ions at the two ends of the channel.

This phenomenon has attracted a lot of interest, due in particular to its potential applications in the context of chemical analysis, for which it would provide a very interesting way of enhancing the sensitivity of detection methods.

At a basic level, the origin of preconcentration is a “cross effect” as introduced in eqn (37): an electric potential drop \( \Delta V \) leads to a flux of ions \( \Phi_i \), as quantified by the cross-mobility \( \mu_K \). According to the PNP result for \( \mu_K = eu \times 2\Sigma/b \), this cross effect is thus a direct consequence of confinement and the existence of surface charges. Accordingly the magnitude of its effect, as compared e.g. to the diffusive flux, depends on the Dukhin number, see eqn (38).

But the detailed mechanisms underlying the preconcentration involve non-linear couplings between the various transport processes of ions in the nanochannel, which are quite complex to rationalize. A systematic description of the phenomenon was proposed by Plecis et al. in ref. 126, revealing the existence of various preconcentration regimes. We refer to ref. 40 for a detailed discussion on the mechanisms underlying this process.

5. More complex functionalities: nanofluidic diodes. The analogy with transport in semiconductors quoted above suggests that more complex nanofluid transport phenomena can be obtained in the regime of Debye layer overlap.

We discuss here the analog of a PN junction in SC transport. Using the equivalence table, Table 1, a PN junction corresponds for nanofluidic transport to a nanochannel exhibiting a disymmetric surface charge along its surface. Such a nanofluidic diode device has been developed by Karnik et al.,6 following a previous work by Siwy et al. in a different pore geometry.3 This is illustrated in Fig. 12 from ref. 6. The surface of a nanochannel is coated with two different surface treatments (half with avidin, half with biotin), leading to a surface charge contrast along the two moieties of the channel, Fig. 12 (left). Accordingly the current \( \text{versus} \) applied electric potential drop characteristics is found to exhibit an asymmetric shape: as in a classical diode, the current passes only in one direction. Similar asymmetric \( I-V \) curves are obtained for pores with asymmetric geometries, like conical pores obtained by track–etch techniques.7

At a more quantitative level, Karnik et al. discussed the effect on the basis of the PNP equations discussed above, under the assumption of local electroneutrality. In the present disymmetric case, Karnik et al. solve numerically these PNP equations for an applied potential drop at the ends of the pore.6 Solutions are shown in Fig. 12, demonstrating that the PNP framework is indeed able to capture the transport rectification measured experimentally.

This diode behavior can also be discussed in the context of the analogy with semiconductor transport that we put forward...

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Fig. 12 Left (a) A nanofluidic diode is fabricated by patterning a nanochannel with different coating on its two moieties (avidin and biotin here). (b) Epifluorescence image of the fabricated nanofluidic diode, showing fluorescently labeled avidin in half the channel. Scale bar 20 \( \mu \)m. Right Current \( \text{versus} \) applied voltage. Symbols are experimental data, while the solid lines are theoretical predictions using a PNP transport model. From ref. 6.
above. The geometry described in Fig. 12 is indeed equivalent to that of a classical PN junction, corresponding to two regions with different doping. In the present case of a nanofluidic diode, the doping contrast between the P and N regions is associated with the different surface charge between the two moieties of the nanochannel. The diode effect in PN junctions is classically interpreted in terms of the Space-Charge Zone at the interface between the two regions with different doping. An approximate solution of the PNP equations can be proposed and leads to a rectified $I-V$ characteristic which takes the form of the so-called Shockley equation

$$I = I_S \left( \exp\left( \frac{eV}{k_B T} \right) - 1 \right)$$

(42)

where $I_S$ is the so-called saturation current. This expression is expected to describe well the blocking to non-blocking transition of the junction, i.e. for moderate $eV/k_B T$. However, this expression strongly overestimates the current at large $eV/k_B T$. For instance, it gives

$$I_S \approx eA n_i^2 \left( \frac{D_n}{L_n \rho_A} + \frac{D_p}{L_p \rho_D} \right)$$

(43)

where $n_i$ is the carrier density, $D_n$, $D_p$ the diffusion coefficients of electrons and holes, and $L_n$, $L_p$ the length of the P and N regions. Using the equivalence table, Table 1, one may convert this expression for the ionic transport using $D_n = D_\text{os}, D_p = D_\text{os}$, $L_n = L_p = L/2$, while $\rho_A = 2 |\Sigma_A|/h$ and $\rho_D = 2 |\Sigma_D|/h$.

This Shockley expression predicts an $I-V$ curve in qualitative agreement with the experimental result in Fig. 12. However, quantitatively it does (very strongly) overestimate the current for large voltages $V$, as expected due to the simplifying assumptions underlying the expression in eqn (42).

The analogy is however interesting to capture the underlying physics behind ion rectification in ionic transport. It allows to describe the full zoology of fluidic functionalities, in line with their SC analogues.

Finally it is interesting to quote that the disymmetry measured here for $I-V$ characteristics generalizes to other transport phenomena. For example, Siwy et al. also demonstrated the occurrence of a disymmetric diffusion of ions through conical pores.128

Altogether these phenomena demonstrate the richness and complexity of behaviors obtained in the regime of Debye layer overlap. This definitely shows the great potential of nanofluidics, where further phenomena should emerge in the future using the benefit of these couplings.

V. Thermal fluctuations

In this section we raise the question of the role of thermal fluctuations in nanofluidic transport. As a general statistical rule, when the size of the system decreases, fluctuations play an increasingly important role. But under which conditions do they play a role? And which role could they play in nanofluidic transport?

There are quite a few studies on this question in relation to nanofluidic transport. One may cite the experimental study of noise in solid state nanopores by Dekker et al.129 The question of thermal fluctuations was also discussed in the context of numerical molecular dynamics simulations of osmotic flow through carbon nanotubes by Hummer et al.130,131 Simulations show that—in the single file regime—the flow rate is essentially governed by thermal fluctuations rather than hydrodynamics. Hummer et al. proposed a 1D random walk to describe the nanofluidic water flow in this stochastic regime. Now, it is fair to remark that fluctuations are indeed expected to play a key role for single file transport, for which dynamics are highly correlated.

Aside from this situation, various indications of the role of thermal fluctuations have been reported, especially in studies involving capillary dynamics. One may cite the noise effects in the breakup of fluid nanotubes by Moseler and Landman,132,133 the noise assisted spreading of drops,134 and the influence of thermal noise in thin film dewetting135 in relation to experiments. In these different cases, thermal noise modifies quite strongly the dynamics, even at relatively large length scales (up to typically 100 nm in ref. 135). These different situations can be described within the framework of fluctuating hydrodynamics,136 in which a random stress tensor is added to the Navier–Stokes terms. While this approach is indeed fruitful in describing the role of thermal fluctuations, a general criterion to quantify the importance of noise is however lacking.

Here, to illustrate the potential importance of fluctuations, we consider a simple situation in which an osmotic flow is driven across a single nanopore. The pore has diameter $d$ and length $L$ and is impermeable to the solute. The pressure drop across the membrane is $\Delta p = k_B T \Delta c$, with $c$ the solute concentration. Under the pressure drop $\Delta p$, a fluid flow is induced, with mean velocity $\bar{v}$. Assuming NS equations hold gives $\bar{v} \sim \frac{\Delta p}{\eta}$. The flow is in the direction of higher solute concentrations.

Now one may ask the question: could fluctuations yield a reverse flow, i.e. against the pressure drop, at least for a short time? This would be clearly a (punctual) violation of the second law. And what is the minimal size at which this may occur? A lead to such questions is provided by the so-called Fluctuation Theorem, which quantifies the probability of second law violation by fluctuations. This domain is presently very active, in particular in the context of single molecule spectroscopy.138 The theorem states that the probability $P(Q_s)$ of finding a value $Q_s$ of the amount of heat dissipated in a time interval $\tau$ satisfies in a non-equilibrium state

$$P(Q_s)/P(-Q_s) = \exp(Q_s/k_B T)$$

(44)

In the nanofluidic situation, this theorem would thus quantify the probability of a flow against the osmotic gradient. Let us compute the order of magnitude for the averaged $Q_s$ in the stationary state: $Q_s \approx F \times \bar{u} \times \tau$, with $F$ the frictional force acting on the nanopore surface. One has $F = \pi d L \sigma_w$, with $\sigma_w$ the stress at the wall given by $\sigma_w \sim d \Delta p / L$. To fix ideas, we compute the amount of heat dissipated over a time needed for...
a molecule to pass through the whole pore, i.e. $\tau = L/\bar{u}$. Altogether this gives

$$Q_0 \sim \Delta p \times \gamma'$$

with $\gamma' = \frac{6\eta L}{r}$ the volume of the pore. According to eqn (44), violations of the second principle are more likely to occur when $Q_0$ is of the order of the thermal energy. Putting in numbers, if we choose $\Delta c = 1$ M (close to physiological conditions), then the condition $Q_0 \sim k_BT$ is obtained for nanometric volumes, i.e. for a pore with a size (diameter, length) typically in the nanometer range. This is indeed typically the order of magnitude for the size of biological pores.

The occurrence of such ‘counter flow’ fluctuations has actually been observed in MD simulations of osmotic flows through carbon nanotube membranes by Hummer et al.,130 and a stochastic model was proposed to account for the water transport across the tube. The above analysis thus fixes the limit where fluctuations starts to be predominant over the mean behavior.

Finally we note that one may perform the same estimate for a different situation of an electric current induced by an electrostatic potential drop $\Delta V$. Assuming a bulk conductance, the dissipated heat is estimated under quite similar terms as $Q_t \sim e\Delta V \times \rho_s \gamma'$, with $\rho_s$ the salt concentration. Again the condition $Q_t \sim k_BT$ is achieved for nanometric volumes.

These results point to the crucial role of fluctuations in pores with nanometric size. This is the typical scale of a biological pore: it is then interesting to point out that biological pores are working at the edge of second law violation ($Q_t \sim k_BT$).

These questions would deserve further experimental and theoretical investigations.

VI. Discussion and perspectives

In this review, we hope to have convincingly shown that nanoscales do indeed play a key role in fluids. A broad panel of length scales ranging from the molecular to the micrometric scales leads to a rich ensemble of nanofluidic phenomena. While the domain of validity of Navier–Stokes equations was shown to extend down to the nanometer scale, specific transport phenomena show up due to the complex couplings which build up between flow and ion transport, electrostatics, surface dynamics, etc.

We focused in this review on the behavior of fluids at the nanoscale. But in doing so we omitted several important topics in the discussions, however strongly connected to nanofluidics questions.

This concerns in particular the field of transport of (macro-) molecules, polymers, polyelectrolytes or biological molecules (DNA, RNA) through nanopores. This involves either biological nanopores, like the widely studied z-haemolysin, or artificial solid-state nanopores made by ionic drilling of membranes.142 Starting from the pioneering work by Bezrukov et al. and Kasianowicz et al., there has been a thorough exploration of the translocation mechanisms of macromolecules in tiny pores, with important implications for the understanding of the biological translocation process and potentially for single molecule analysis. This domain is now rapidly expanding and we refer to the recent review by Dekker for further reading.142

Another aspect that we left aside is the question of nano- and micro-structured surfaces, in line with the recently developed super-hydrophobic surfaces exhibiting the Lotus effect. Superhydrophobic coatings can lead to huge slippage effects, with slip lengths in the micrometer range, as well as other dynamic phenomena, such as hydro-elastic couplings at the superhydrophobic interface.147 Such surfaces offer the possibility to considerably enhance the efficiency of transport phenomena in particular in the context of slip enhancement discussed above. For example, as we pointed out in the text, a massive amplification, by a factor up to $10^4 (!)$, is predicted for diffusio-osmosis on superhydrophobic surfaces, which offers the possibility to devise efficient salt pumps.114 The underlying coupling mechanisms remain however subtle, and this enhancement was shown for example to break down for electro-osmotic transport.114 The implications of nano- and micro-structuration on fluidic transport is still at its infancy and remains to be thoroughly explored. It offers the possibility of coupling fluid dynamics over the scales, from the nano- to the micro-scales, and even to larger macroscopic scales.149

Furthermore, beyond these questions, it is interesting to note that nanofluidics offers the possibility of attacking old questions with new points of views, and new control possibilities. We quoted the amazing flow permeability measured by carbon nanotube membranes. While this performance remains to be understood—and possibly investigated at the individual nanotube level—this opens up very promising application in the field of energy, in particular for portable energy sources. Such membranes indeed offer the possibility of very efficient conversion of hydrostatic energy to electrical power at small scales, see also ref. 150. As we have discussed above, low (nanoscale) friction at surfaces considerably amplifies electrokinetic processes, such as electro-osmosis or streaming currents.100,103 The latter phenomenon is able to produce an electrical current from a pressure drop.151,152 On this basis it was argued that the efficiency of this mechano-electric transduction increases considerably for slippery walls: reasonable values suggest an increase of the energy conversion efficiency from a few percent to 30% for slippery surfaces! While the tremendous effect of low surface friction and slippage on charge transport has been recently confirmed experimentally, its expected impact on mechano-electric energy conversion has not received experimental confirmation. Extrapolating with the results obtained with the nanotube membranes, this power conversion efficiency increases to close to 100% (due to the expected extremely weak dissipation) and this amazing prediction would lead to a production of electrical power of several kW m$^{-2}$ for a pressure drop of 1 bar. This is an impressive result, which has not been confirmed up to now. While such predictions have to be taken with care, they strongly suggest exploring the role of nanofluidics in the context of energy conversion. Such nanofluidic energy conversion devices have a priori the potential to power larger scale systems (for example in cars or portable devices), due to their high power density and low weight.1
An alternative field of application for progress made in nanofluidic transport is desalination. Indeed, as half of humanity has no immediate access to potable water, desalination of seawater has emerged over recent years as an alternative solution to developing fresh water. Reverse osmosis is one of the techniques used in this context, for example in the Ashkelon plant in Israel,153 seawater is pushed through a membrane impermeable to the salt. Such a process is expensive (typically around 0.5 $/m^3 for the Ashkelon plant153), due—among other factors—to the energy required for this operation. The possibility of reducing this energy by using a considerably more permeable membrane should therefore have a direct impact on the cost of produced water. This is a potential more permeable membrane should therefore have a direct impact on agriculture and health. For example the concentration of boron (B), which is toxic to many crops, is high in seawater, and requires to be partially eliminated by desalination post-treatments.153 Reversely, desalination removes some ions which are essential to plant growth, such as Mg^{2+} or SO_4^{2-}. There is therefore a potential need for better selectivity of filtration.

Achieving selectivity similar to biological channels, such as aquaporins,8,11,12 is still out of reach, but nanofluidics has a major role to play in this context in order to find the key tuning parameters and architecture. Such applications may still be years away, but the basic principles underlying their operation will develop in the years to come.

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154 “Par ma foi! il y a plus de quarante ans que je dis de la prose sans que j’en susse rien, et je vous suis le plus obligé du monde de m’avoir appris cela.”, which translates into “By my faith! For more than forty years I have been speaking prose without knowing anything about it and I am much obliged to you for having taught me that”.
155 We specifically thank D. Stein for very interesting discussions concerning this point.
156 We choose here to define the zeta potential as the one appearing in the Smoluchowski formula. According to eqn (20), this may differ from the surface potential, depending on conditions. Another possibility would have been to define the zeta potential as \( V_0 \) and consider an amplified electro-osmotic mobility. We preferred to use the former definition.