We theoretically consider the possibility of using electric fields in aqueous channels of cylindrical and planar geometry to induce transport in the absence of mobile ionic charges. Using the Navier–Stokes equation, generalized to include the effects of water spinning, dipole orientation and relaxation, we show analytically that pumping of a dipolar liquid through an uncharged hydrodynamic channel can be achieved by injecting torque into the liquid, based on the coupling between molecular spinning and fluid vorticity. This is possible using rotating electric fields and suitably chosen interfacial boundary conditions or transiently by suddenly switching on a homogeneous electric field. A static electric field, however, does not induce a steady state flow in channels, irrespective of the geometry. Using molecular dynamics (MD) simulations, we confirm that static fields do not lead to any pumping, in contrast to earlier publications. The pumping observed in MD simulations of carbon nanotubes and oil droplets in a static electric field is tracked down to an imprudent implementation of Lennard-Jones interaction truncation schemes.

Introduction

Efficient conversion of energy from one form to another is nowadays a pressing issue. In fluidic applications, this mainly comes down to conversion between electrical and mechanical energy: the key elements of fluidic systems are pumps for converting electrical power into a hydrostatic pressure difference and turbines or electro-osmotic power generators for the reverse process. The realization of the full potential of laboratory miniaturization depends crucially on the design and fabrication of these active fluidic components on the nanoscale. In particular, pumps are of critical importance for the two principal functionalities of chip-sized laboratories: transport and mixing.1,2

It has long been recognized that electro-osmosis is a very efficient and scalable mechanism to use in nanoscale pumps.3 The classical electro-osmotic pump is based on a charged surface and operated with ionic solutions. Under influence of an electric field, the ions move along the surface and drag the fluid along. Alternatively, electro-osmotic pumping can be achieved at a neutral channel surface with a salt solution of which the cations and anions have different affinities for the surface.4,5 In this case, the asymmetric distribution of ions generates a finite torque in the interfacial liquid layer, causing the fluid to move in one direction.

The use of carbon nanotubes as channels and pumps in nanofluidic devices has been a major aim for the nanofluidic community ever since the discovery that water moves almost frictionless through carbon nanotubes.6,7 However, the fact that nanotubes are uncharged limits the possibilities for the use as active electro-osmotic components. Different ways of pumping fluid with carbon nanotubes have been suggested. Using molecular dynamics simulations, Insepop et al. demonstrated that gas molecules can be moved peristaltically through a nanotube under influence of a traveling acoustic wave.8 A little later, Longhurst and Quirke showed that a temperature gradient moves decane molecules through a nanotube, also using molecular dynamics simulations.9 A slightly different method was proposed by Kril and Tománek, making use of the semiconducting properties of nanotubes to move particles through the tube due to the coupling to laser-excited propagating electrons.10

Many examples of efficient nanoscale pumps and channels are found in nature, where different protein channels transport water, ions and macromolecules in a highly specific manner across membranes.11,12 A synthetic channel exhibiting some of the selective transport and fast flow properties of biological channels would have a wide range of possible applications, not only for pumping, but also for filtering and desalination. To realize this goal, Gong et al. designed a nanotube with a fixed external charge distribution mimicking the charge distribution on an aquaporin channel. In molecular dynamics simulations, they observe a finite water flow through the tube.13,14 Fixed charges outside a carbon nanotube also influence the pressure-driven passage of water molecules.15 Finally, uncharged channels filled with solutions of the relatively symmetric salts sodium chloride or potassium chloride are found to exhibit electro-osmotic flow.16–18

The pumping efficiency and performance of electrokinetically driven channels can be expressed in terms of the ζ-potential, which is a material property defined by the Helmholtz–Smoluchowski equation

\[
\zeta = -\frac{\eta u}{\varepsilon_0 E}
\]

(1)

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with η the shear viscosity, εε the permittivity, E the electric field, and u the bulk fluid velocity in the direction of E. According to standard theory, a nonzero ζ-potential arises only in the presence of mobile charged species, which limits the use of electrokinetic effects in uncharged nanochannels. However, the ζ-potential of solutes in water has been a source of controversy for many years.19–21 Ever since the first electrophoretic measurements it has been known that nominally uncharged substances like air bubbles and oil droplets in pure water exhibit a negative ζ-potential.22 Generally, this negative ζ-potential of uncharged solutes is attributed to the accumulation of negatively charged ions at the solute surface.23–25 In contrast with this traditional view, a recent simulation study reports nonzero ζ-potentials for heptane droplets in pure H2O without mobile ions.26 Similarly, several molecular dynamics simulations show electro-osmotic flow in hydrophobic channels without mobile charged species: Joseph and Aluru report flow in a carbon nanotube under a constant electric field27 and Gong et al. report flows in carbon nanotubes induced by fixed charges outside the nanotube.13 Most of these simulations,25,28,29 the results of which we will critically re-evaluate in this paper, have been performed using the molecular dynamics simulation package GROMACS.29 Apart from their ability to specifically adsorb different ions, aqueous interfaces have a strong ordering effect on the first few molecular layers next to the interface. The outermost interfacial water layer is itself oriented, giving rise to a considerable dipole density.27 This structured water next to the interface has a profound influence on the dielectric properties, the viscosity, and the interaction with ions, among many other surface characteristics.3,29 In an attempt to rationalize the surprising simulation results exhibiting electrokinetic effects at uncharged aqueous interfaces, the coupling of the electric field to the dipolar surface layer was speculated to provide an alternative mechanism for the appearance of a nonzero ζ-potential, inducing flow through rotation of the ordered water molecules.24,25

In this paper we discuss two central questions: First, can the dipolar ordering of the water surface layer give rise to a nonzero ζ-potential in a static and uniform electric field? And second, can the dipolar nature of water be exploited for electro-hydraulic power conversion, and in that way enable the use of uncharged channels as active electrokinetic components? We show that using a static electric field, electro-osmotic pumping of pure water in a planar or cylindrical hydrophobic channel is impossible. This result, which is confirmed by extensive molecular dynamics simulations, comes from an analysis based on a generalized Navier–Stokes formulation that includes angular momentum in the form of spinning molecules as well as dipolar ordering and relaxation. Employing rotating electric fields combined with suitable boundary conditions, on the other hand, the coupling between molecular rotation and vorticity can be used to pump a dipolar fluid through a nanofluidic channel. A partial account of this work has been published in ref 29.

**Generalized Navier–Stokes Approach**

**Conservation of Angular Momentum.** If an internal force \( \vec{F}_{\text{int}} \) acts on some element of a continuum, stress builds up that is described by a nonvanishing stress tensor \( \vec{P} \) for which \( \rho \partial \vec{u} / \partial t = \vec{F}_{\text{int}} \), with \( \vec{F}_{\text{int}} \) the surface area of the element and \( \vec{u} \) the vector normal to the surface. Note that in the following we denote \( \vec{P} \) as the shear stress tensor in order to distinguish it from the stress tensor associated with the spinning of molecules. The shear stress tensor can be split into a part corresponding to the hydrostatic pressure \( \rho \) and a friction part \( \vec{F} \), which in turn can be split into a symmetric part \( \vec{F}_{\text{sym}} \) and an antisymmetric part \( \vec{F}_{\text{asy}} \),

\[
\vec{P} = -\rho \vec{U} + \vec{F}_{\text{asy}} \quad \text{and} \quad \vec{F}_{\text{sym}} = \vec{F}_{\text{asy}} + \vec{F}_{\text{asy}}^T
\]

with \( \vec{U} \) the unit tensor. For a monatomic fluid the antisymmetric part \( \vec{F}_{\text{asy}} \) of the shear stress tensor is zero. In a polar fluid, the interaction between two points in the fluid is not only modeled via the internal force vector and the associated stress tensor, but also via the torque per unit mass \( \vec{F}_{\text{int}} \). Equivalent to Cauchy’s stress principle for the force \( \vec{F}_{\text{int}} \), there is a spin stress tensor \( \vec{C} \) for which \( \vec{C} \rho \partial \vec{u} / \partial t = \vec{dF}_{\text{int}} / \partial t \) holds. The total rate of change of the angular momentum per unit mass \( \vec{L} \), integrated over a material volume \( V \), can be written as

\[
\int \rho \partial \vec{L} / \partial t \; dV + \int \rho \vec{L} \partial \vec{u} / \partial t \; dA = \int \vec{F}_{\text{asy}} \; dV
\]

with \( \vec{u} \) the velocity of the molecules and \( \rho (\vec{x}, t) \) the mass density. The material derivative \( d/dt \) is defined as \( d/dt = \partial / \partial t + \vec{u} \cdot \nabla \). These considerations lead to the following balance equation for the total rate of change of \( \vec{L} \),

\[
\int \rho \partial \vec{L} / \partial t \; dV = \int \rho (\vec{T} + \vec{x} \times \vec{F}) \; dV + \int \vec{u} \cdot (\vec{C} + \vec{x} \times \vec{P}) dA = \int (\vec{T} + \vec{F} + \nabla \cdot \vec{C} + \nabla \cdot (\vec{x} \times \vec{P} \; dV)
\]

where \( \vec{C} \) is the antisymmetric part of the shear stress tensor in axial vector representation and \( \vec{P} \) denotes the transpose of the tensor \( \vec{P} \). Rearranging the last term on the right-hand side of eq 4 yields \( \nabla \cdot (\vec{x} \times \vec{P}) + 2 \Pi_{\text{asy}}^a \), where

\[
\Pi_{\text{asy}}^a = \frac{1}{2} \epsilon_{\beta \alpha} \Pi_{\beta \alpha}^a
\]

is the antisymmetric part of the shear stress tensor in axial vector representation and \( \vec{P}^T \) denotes the transpose of the tensor \( \vec{P} \). Realizing that eq 4 holds for any volume \( V \) yields the local conservation of total angular momentum:

\[
\rho \frac{d \vec{L}}{dt} = \rho (\vec{T} + \vec{x} \times \vec{F}) + \nabla \cdot \vec{C} + \vec{x} \times (\nabla \cdot \vec{P}^T) + 2 \Pi_{\text{asy}}^a
\]

The total angular momentum can be written as the sum of the vorticity contribution \( \vec{x} \times \vec{u} \) and a spin contribution \( \vec{I} \cdot \vec{\omega} \), accounting for molecular rotations,

\[
\vec{L} = \vec{x} \times \vec{u} + \vec{I} \cdot \vec{\omega}
\]

with \( \vec{I} \) the moment of inertia per unit mass and \( \vec{\omega} \) the average angular velocity of the constituent particles. The moment of inertia \( \vec{I} \) is a tensor depending on the mass distribution within the particles and on the local orientational distribution. Because of the approximate mass isotropy of the water molecules, the tensor \( \vec{I} \) is almost diagonal even if the orientational distribution of water molecules is very anisotropic, as happens to be the case close to an interface.30 We therefore take \( \vec{I} \) to be a diagonal tensor with

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value \( I \). For the first part of eq 6 we write down a separate conservation law, starting from the conservation law for linear momentum,

\[
\rho \frac{d\vec{u}}{dt} = \rho \vec{F} + \nabla \cdot \vec{P}
\]

(7)

We take the vectorial product of \( \vec{x} \) with eq 7, leading to

\[
\rho \frac{d}{dt}(\vec{x} \times \vec{u}) = \rho (\vec{x} \times \vec{F}) + \vec{x} \times (\nabla \cdot \vec{P})
\]

(8)

The difference between eqs 5 and 8 gives the conservation law for the spin part of the angular momentum density:

\[
\rho I \frac{d\vec{\omega}}{dt} = \rho \vec{\Gamma} + \vec{\nabla} \times \vec{C} + 2\vec{\Pi}^\omega
\]

(9)

To leading order, \( \vec{C} \) only depends on \( \vec{\omega} \). Equation 9 then shows that, to leading order, the only coupling between the vorticity part and the spin part of the angular momentum comes from the antisymmetric part of the shear stress tensor \( \vec{\Pi}^\omega \).

**Material Equations.** We now derive expressions for the terms occurring on the right-hand side in eq 9. If two neighboring fluid elements moving with velocity \( \vec{u} \) are rotating each with the angular velocity

\[
\vec{\omega} = \frac{1}{2} \vec{\nabla} \times \vec{u}
\]

the internal spin and the vorticity are synchronized, and no stress results. The antisymmetric part of the shear stress tensor should therefore be a function of

\[
\frac{1}{2} \vec{\nabla} \times \vec{u} - \vec{\omega}
\]

Additionally, \( \vec{\Pi}^\omega \) should vanish when \( \vec{\nabla} \times \vec{u} = 2\vec{\omega} \), and \( \vec{\Pi}^\omega \) should have the same direction as \( \vec{\nabla} \times \vec{u} - 2\vec{\omega} \). Therefore, to leading order we can write

\[
\vec{\Pi}^\omega = \eta(\vec{\nabla} \times \vec{u} - 2\vec{\omega})
\]

(10)

with \( \eta \) being the vortex viscosity. To leading order, the spin stress tensor \( \vec{C} \) should depend on spatial differences in the spin field \( \vec{\omega} \) only. By equilibrating the second moments of the force, the spin stress tensor can be proven to be symmetric.\(^{32}\) Disregarding higher derivatives as for the shear stress tensor we write

\[
C_{ij} = \nu \nabla_k \omega_k \delta_{ij} + \nu \left( \nabla_i \omega_j + \nabla_j \omega_i - \frac{2}{3} \nabla \omega \delta_{ij} \right)
\]

(11)

with \( \nu \) being the spin viscosity and \( \nu \) the volume spin viscosity and using the Einstein summation convention. Combining eqs 9, 10, and 11 yields

\[
\rho I \frac{d\vec{\omega}}{dt} = \rho \vec{\Gamma} + 2\eta(\vec{\nabla} \times \vec{u} - 2\vec{\omega}) + \nu \Delta \vec{\omega} + (\nu + \nu_3/3) \vec{\nabla} \cdot \vec{\omega}
\]

(12)

The flow velocity is described by the Navier–Stokes equation for incompressible fluids in the absence of a body force

\[
\rho \frac{d\vec{u}}{dt} = -\nabla p + \eta \Delta \vec{u} - \eta \vec{\nabla} \times (\vec{\nabla} \times \vec{u} - 2\vec{\omega})
\]

(13)

with \( p \) the hydrostatic pressure and \( \eta \) the shear viscosity.

---


**General Stationary Solution For Planar Substrates.** Considering a rectangular geometry with the fluid confined in a slab between two surfaces, as sketched in Figure 1a, both the velocity and spin field depend only on \( x_3 \) because of translational invariance along the \( x_1 \) and \( x_2 \) directions. Additionally, because of incompressibility, the velocity is restricted to the \( x_1 \) direction, leading to \( \vec{u} = \hat{e}_1 u_1(x_3) \) and \( \vec{\omega} = \vec{\omega}(x_3) \). Thus, the only nonzero component of the vorticity \( \vec{\nabla} \times \vec{u} \) is the \( x_2 \)-component. In steady state, eq 12 reduces to

\[
\begin{align*}
0 &= \rho \Gamma_1 + \nu \nabla_3^2 \omega_1 - 4\eta \omega_1 \\
0 &= \rho \Gamma_2 + \nu \nabla_3^2 \omega_2 + 2\eta(\nabla_3 u_1 - 2\omega_2) \\
0 &= \rho \Gamma_3 + \nu \nabla_3^2 \omega_3 - 4\eta \omega_3 + (\nu + \nu_3/3) \nabla_3^2 \omega_3
\end{align*}
\]

(14)

so if no torque is applied in \( x_1 \) and \( x_2 \) direction, the angular velocity in these directions is zero. Assuming spatially constant pressure along \( x_1 \), we work out eq 13 for the assumptions mentioned above and integrate once over \( x_3 \), leading to

\[
(\eta + \nu) \nabla_3 u_1 = 2\eta \omega_2 + c_1 (\eta + \nu)
\]

(15)

where \( c_1 \) is an integration constant that has to be determined from the boundary conditions. Equation 15 indicates that the vorticity arising from molecular rotation is a linear function of the angular velocity of the molecules. Inserting eq 15 in the \( x_3 \) component of eq 14 yields the following differential equation for \( \omega_2 \)

\[
0 = \rho \Gamma_2 / \nu + (\nabla_3^2 - k^2) \omega_2 + 2c_1 \eta \omega_2 / \nu
\]

(16)

with

\[
k^2 = 4\eta \omega_2 / [\nu(\eta + \nu)]
\]

(17)

for arbitrary torque \( \Gamma_2 \). If \( \Gamma_2 \) has a spatial dependence, but is independent of \( \omega_2 \), eq 16 has the following solution

\[
\omega_2(x_3) = c_2 e^{k x_3} + c_3 e^{-k x_3} + \int_{-\infty}^{x_3} \frac{\rho \Gamma_2(x')}{k^2 \nu} e^{-k(x_3 - x')} dx'
\]

(18)

where the constants \( c_i \) are determined by boundary conditions. The flow profile follows from eq 15 as

\[
\begin{align*}
\theta_1(x_3) &= c_1 x_3 + \frac{\nu}{2\eta} \left[ e^{k x_3} - e^{-k x_3} + \frac{c_2}{k} + \frac{c_4}{k} \right] \\
&+ \int_{-\infty}^{x_3} \frac{\rho \Gamma_2(x')}{2k^2 \nu} e^{-k(x_3 - x')} dx' dx_3
\end{align*}
\]

(19)

**Torque from a Static Uniform Electric Field.** The \( \zeta \)-potential is given by the bulk fluid flow induced in the direction of a static electric field. To solve eq 16 for this situation, we calculate the torque \( \vec{\Gamma} = \vec{\mu} \times \vec{E} \) for a constant electric field \( E_0 \) in

---

**Figure 1.** Sketch of the rectangular (a) and cylindrical geometry (b).
the $x_1$ direction. We model the dipolar ordering of the interfacial water layer by an additional $x_1$ dependent electric field $E_i^0(x_3)$ in the $x_3$ direction. This field accounts for the interaction between neighboring water molecules and plays the role of the crystal field that is used in ordinary mean-field theory for magnetic systems. The total electric field in the system becomes $\vec{E} = \vec{e}_1 E_i^0(x_3) + \vec{e}_3 E^0$. The linear evolution equation for the polarization density $\vec{p} = \vec{p}(x_3)$ is given by

$$\frac{\partial \vec{p}}{\partial t} = \frac{1}{\tau} (\alpha \vec{E} - \vec{p}) + \vec{\omega} \times \vec{p}$$

with $\tau$ the relaxation time of the orientation and $\alpha$ the polarizability per unit mass. Because of translational invariance and directional symmetry in the $x_2$ direction, the dipole moment in the $x_3$ direction vanishes: $\mu_2 = 0$. Since also $E_2 = 0$, it follows that the torque $\Gamma_1 = \Gamma_2 = 0$, and therefore $\omega_1 = \omega_2 = 0$ by virtue of eq 14. Equation 20 can be solved for $\vec{p}$ in the steady state:

$$\mu_1 = \frac{\alpha E_i^0 + \tau \omega_2 \alpha E_i^0}{1 + \tau^2 \omega_2^2}$$

and

$$\mu_3 = \frac{-\alpha E_i^0 - \tau \omega_2 \alpha E_i^0}{1 + \tau^2 \omega_2^2}$$

For the torque density, it follows

$$\Gamma_2 = -\frac{\tau \omega_2 \alpha (E_i^0 + E_i^0)}{v(1 + \tau^2 \omega_2^2)} + (\nabla \cdot \vec{E}) \omega_2 + 2 \zeta \eta_v$$

Inserting eq 22 into eq 16 yields

$$0 = -\frac{\tau \omega_2 \alpha (E_i^0 + E_i^0)}{v(1 + \tau^2 \omega_2^2)} + (\nabla \cdot \vec{E}) \omega_2 + 2 \zeta \eta_v$$

Strikingly, eq 23 is quadratic in the external field strength $E_i^0$, which means that switching the sign of $E_i^0$ leaves the equation invariant. Also, since $c_1$ is an arbitrary integration constant only subject to the spinning boundary conditions at the surface, the sign of $\omega_2$ is undetermined, meaning that a nonzero value of $\omega_2$ would require a spontaneous symmetry breaking, which seems unphysical. In fact, it can be shown that in hydrodynamics, the stable solution corresponds to the solution of minimal dissipation or minimal entropy production, which is obviously the solution corresponding to $\omega_2 = 0$. Therefore, the only physical and also stable solution is the one corresponding to a vanishing spin field, $\omega_2 = 0$ and thus the integration constant $c_1$ also vanishes, $c_1 = 0$. If $\omega_2 = 0$, the vorticity also vanishes according to eq 15, and no flow results. From the Helmholtz–Smoluchowski equation (eq 1) it is directly evident that this means that neutral solutes in a purely dipolar fluid without mobile charges have zero $\zeta$-potential. This stands in contrast with a few published molecular dynamics simulation results, as mentioned in the introduction, and will be discussed and confirmed by molecular dynamics simulations further below.

**Polarization Density for a Homogeneous Time Dependent Electric Field.** For time-dependent electric fields, the time derivatives on the left-hand sides of eqs 12 and 13 do not vanish. For homogeneous fields, however, all substantial time derivatives reduce to partial time derivatives, due to the assumption that $u_t(x_3, t)$ is the only component of the fluid velocity. Again, we consider the case where no electric field is applied in the $x_3$ direction, and $\mu_2 = 0$ due to symmetry and translational invariance. Because from eq 14 it follows that $\omega_1 = \omega_2 = 0$, the equations for the polarization density (eq 20) reduce to

$$\frac{\partial \mu_1}{\partial t} = \frac{1}{\tau} (\alpha E_1 - \mu_1) + \omega_3 \mu_3$$

$$\frac{\partial \mu_3}{\partial t} = \frac{1}{\tau} (\alpha E_3 - \mu_3) - \omega_2 \mu_1$$

Via $\omega_2$, changes in the polarization in the $x_1$ direction are coupled to changes in the $x_3$ directions and vice versa, so we have to solve the whole system of equations simultaneously. The homogeneous solution ($\vec{E} = 0$) to eq 24 equals

$$\mu_1(x_3, t) = e^{-it/\tau} (C_1 \sin \Omega_2 + C_2 \cos \Omega_2)$$

$$\mu_3(x_3, t) = e^{-it/\tau} (C_1 \cos \Omega_2 - C_2 \sin \Omega_2)$$

with $C_1$ denoting integration constants and

$$\Omega_2 = \int_0^t \omega_2(x_3, t') \, dt'$$

The particular solutions of eq 24 depend on the electric field applied.

**Torque from an Electric Field Step Function.** For an electric field $E_i^0(x_3)$ in the $x_3$ direction that is constant in time and a spatially constant field in the $x_3$ direction of strength $E_i^0$ that is switched on at $t = 0$, the particular solution is a constant dipole density, leading to the full solution

$$\mu_1(x_3, t) = e^{-it/\tau} (C_1 \sin \Omega_2 + C_2 \cos \Omega_2) + \frac{\alpha E_i^0 + \alpha \omega_2 E_i^0(x_3)}{1 + \tau^2 \omega_2^2}$$

$$\mu_3(x_3, t) = e^{-it/\tau} (C_1 \cos \Omega_2 - C_2 \sin \Omega_2) + \frac{\alpha E_i^0(x_3) - \alpha \omega_2 E_i^0}{1 + \tau^2 \omega_2^2}$$

We determine $C_1$ and $C_2$ from the initial conditions: $\mu_1 = 0$ and $\mu_3(x_3) = \alpha E_i^0(x_3)$ at $t = 0$, giving nonzero expressions for both $C_1$ and $C_2$:}

$$C_1 = \frac{\alpha E_i^0(x_3) \omega_2(x_3, 0)}{1 + \tau^2 \omega_2^2}$$

$$C_2 = \frac{-\alpha E_i^0(x_3) - \alpha \omega_2(x_3, 0) E_i^0}{1 + \tau^2 \omega_2^2}$$

with $\omega_2(x_3, 0)$ denoting the spin field at $t = 0$. The torque density $\Gamma_2 = \mu_3 E_i - \mu_1 E_3$ becomes

$$\Gamma_2 = e^{-it/\tau} [\mu_1 E_i^0(x_3) - C_2 E_i^0(x_3)] \cos \Omega_2 - (C_2 E_i^0(x_3) + C_1 E_i^0) \sin \Omega_2 - \frac{\alpha \omega_2 E_i^0 + E_i^0}{1 + \tau^2 \omega_2^2}$$

The conservation law for the angular momentum (eq 12) and the Navier–Stokes equation (eq 13) form another set of coupled partial differential equations which are difficult to solve in the general case. However, considering the fact that $\Gamma_2$ contains both sines and cosines of $\Omega_2$, it is clear that $\omega_3(x_3, t) = 0$ is no longer a solution. For $t \to \infty$, eq 29 reduces to the torque from a constant electric field (eq 22), and the flow vanishes. In conclusion, switching on a constant electric field will only give rise to a transient pumping effect that quickly fades away.

**Torque from a Rotating Electric Field.** Continuous pumping of a fluid can only be achieved when a steady state torque is injected into the system. The easiest way to apply a steady state
torque on a dipolar fluid is using a rotating electric field. Adding an electric field that is rotating in the $x_3$ plane to the dipolar ordering field $E_{x}^2$, the total electric field is given by

$$E_1 = E_r \sin \gamma t \quad \text{and} \quad E_3 = E_r \cos \gamma t + E_{x}^2(x_3)$$

(30)

with $\gamma$ the frequency and $E_r$ the amplitude of the rotating field. Again, we assume $\bar{u} = \bar{e}_3 h_3(x_3)$ and $\omega = \omega(x_3)$. Because of the combination of the rotating field and the time-independent field $E_{x}^2$, the torque and, therefore, the spin and velocity fields depend on time. This time dependence, however, is a periodically varying contribution to otherwise constant quantities. Because we are not interested in the short-time scale behavior of the flow, we time-average eqs 12 and 13 over one cycle of the rotating field, leading to the analogous of eqs 14 and 15 containing the time-averaged quantities $\bar{\Gamma}_3(x_3)$, $\bar{\omega}_2(x_3)$, and $\bar{\pi}_1(x_3)$. Inserting the rotating electric field into eq 20 for the time evolution of the dipole moment we find the following solution

$$\mu_1(x_3, t) = aE_r \cos \phi \sin(\gamma t - \phi) + \frac{aE_r^2 \omega_2 r}{1 + \omega_2^2 r^2}$$

$$+ e^{-t/C}(C_1 \cos \omega_2 t + C_2 \sin \omega_2 t)$$

$$\mu_3(x_3, t) = aE_r \cos \phi \sin(\gamma t - \phi) + \frac{aE_r^2 \omega_2}{1 + \omega_2^2 r^2}$$

$$+ e^{-t/C}(C_2 \cos \omega_2 t - C_1 \sin \omega_2 t)$$

(31)

using the definition $\phi = \arctan[(\gamma - \omega_2)r]$ and where $\omega_2$ depends on $x_3$, and $C_1$ and $C_2$ are constants that can be determined from the initial conditions. Therefore, if the field has persisted for a sufficient amount of time, the dipole density will follow the electric field with a phase difference $\phi$. The time-averaged torque density is given by

$$\bar{\Gamma}_3 = \frac{\gamma}{2\eta} \int_0^{2\pi/\gamma} (\mu_3 E_1 - \mu_1 E_3) \, dt$$

(32)

Inserting $E$ from eq 30 and $\mu$ from eq 31, we find in the long-time limit

$$\bar{\Gamma}_3 = \frac{\alpha aE_r^2 (\gamma - \omega_2) r}{1 + (\gamma - \omega_2)^2 r^2}$$

$$+ \frac{\alpha aE_r^2 \omega_2 r}{1 + \omega_2^2 r^2}$$

(33)

The appearance of $E_{x}^2$ in the equation for the time-averaged torque comes from the fact that the spin field couples the dipole density in the $x_3$ direction to the dipole density in the $x_3$ direction. Because $E_{x}^2$ depends on $x_3$, the equation for $\bar{\omega}_2$ (eq 16 with $\bar{\Gamma}_3$ and $\omega_2$ replaced by $\bar{\Gamma}_3$ and $\omega_2$ respectively) does not have an analytical solution anymore. To proceed, we first solve for $\bar{\pi}_1$ analytically using a perturbative approximation for the torque, afterward we solve for $\bar{\pi}_1$ numerically.

**Perturbative Analysis.** For the sake of power counting we assume the electric fields $E_r$ and $E_{x}^2$ to be of order $E$. Because the polarization density $\bar{\mu}$ depends linearly on the electric field, the torque density $\bar{\Gamma} = \bar{\mu} \times E$ is proportional to $E^2$. To leading order, the spin field $\omega_2$ is proportional to the torque density $\bar{\Gamma}_3$, and therefore also of order $E^2$. Performing a perturbation analysis of eq 33 in powers of $E$ yields to leading order

$$\bar{\Gamma}_3 = \frac{\alpha aE_r^2 \gamma r}{1 + \gamma^2 r^2} + o(E^4)$$

(34)

The effect of the ordering field $E_{x}^2$ is of fourth order in the electric field strength and therefore negligible compared to the leading second order. Nevertheless, pumping of fluid is only possible through surface effects: if the molecules at the boundary are completely free to spin, no momentum will be transferred and no pumping will occur. Obviously, the surface dipolar orientation has a major influence on the spin field at the wall, and neglecting it eliminates most of the interesting physics. Therefore, in the following analysis we include the surface effects of the dipolar order through the boundary condition for the spin field. With eq 34, eq 16 has the following solution

$$\bar{\pi}_2 = \frac{\rho T_2 + 2 \eta c_1}{\nu K^2} + c_2 e^{x_{31}} + c_3 e^{-x_{31}}$$

(35)

with integration constants $c_i$. Using eq 15 we finally obtain

$$\bar{\pi}_1 = \left[ \frac{\rho T_3 + 2 \eta \bar{c} + \eta}{2 \eta} \right]_{x_3} + \nu K^2 \left[ \frac{c_2}{K} e^{x_{31}} - \frac{c_3}{K} e^{-x_{31}} + c_4 \right]$$

(36)

**Boundary Conditions.** Equation 36 contains four integration constants. At each channel wall, positioned at $x_3 = \pm h$, there are two boundary conditions: one for the velocity field and one for the spin field. We assume that the velocity at the wall linearly depends on the local shear stress

$$\bar{\tau}_{b \pm} \nabla_3 \bar{\pi}_1 |_{\pm h} = \bar{\pi}_1 |_{\pm h}$$

(37)

where $b$ is commonly referred to as the slip length, with $b_-$ the slip length at the lower plate and $b_+$ at the upper plate. For the spin boundary condition, we introduce the spin slip length $\xi$

$$\bar{\tau}_{s \pm} \nabla_3 \bar{\pi}_2 |_{\pm h} = \bar{\pi}_2 |_{\pm h}$$

(38)

with $s_-$ the spin slip length at the lower plate and $s_+$ at the upper plate. In a microscopic description, the spin slip length will be largely determined by the restriction on the spinning of the molecules at the wall imposed by orienting interactions with the wall and by the interaction between neighboring interfacial water molecules. On the hydrodynamic theory level, we treat the slip lengths as free parameters.

**Symmetric Boundaries.** For symmetric boundary conditions $b_- = b_+ = b$ and $s_- = s_+ = s$, eq 36 gives the following result

$$\bar{\pi}_1 = \left\{ \Theta [\mathbf{k} b (\cos k \mathbf{h} + \sinh k \mathbf{h}) x_3 - (b + h) \sinh k \mathbf{h} x_3] + (\eta/\eta) b (\cos k \mathbf{h} - \sinh k \mathbf{h} + (b + h) k^2 \sinh k \mathbf{h} \mathbf{k}) \right\}$$

(39)

with the typical frequency (or shear rate) defined by the parameter combination

$$\Theta = \rho aE_r^2 \gamma r / [\eta (1 + \gamma^2 r^2)]$$

(40)

From eq 39 and the expression for $\Theta$ it follows that the largest amplitude of the flow profile is achieved for $\gamma r = 1$, which means


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for a driving frequency that equals the dipolar relaxation frequency. From calculations and molecular dynamics simulations it is known that the spin viscosity $\eta_s$ is an order of magnitude smaller than the shear viscosity $\eta$.\textsuperscript{35,36} In the limit $\eta_s \ll \eta$, eq 39 reduces to

$$\Pi_1 = \Theta \left( \frac{(kh \cosh kh + \sinh kh)x_3 - (h + h) \sinh kx_3}{2k(h + k) \sinh kh} \right)$$

(41)

Clearly, the spin slip length $s$ only changes the magnitude of the flow, and not the flow profile. Taking $s = 0$, which is reasonable in view of the strong orienting field at the boundary, and $b = 0$, corresponding to hydrophilic boundaries, eq 41 can be further simplified to yield

$$\Pi_1 = \Theta \left( \frac{x_3 \sinh kh - h \sinh kx_3}{2kh \cosh kh} \right)$$

(42)

In parts a and b of Figure 2, the flow profile of eq 42 is shown as a solid line for channels of rescaled height $kh = 3$ and $kh = 30$ respectively. Taking $s = 0$ and $b \to \infty$, corresponding to hydrophobic surfaces with infinitely large slip length, on the other hand, eq 41 simplifies to

$$\Pi_1 = \Theta \left( \frac{x_3 \sinh kh - \sinh kx_3}{2 \cosh kh} \right)$$

(43)

as shown in Figure 2, parts c and d. It is easy to see that for all symmetric channels, the integrated flux $\Phi$ vanishes and the net pumping is zero:

$$\Phi = \int_{-h}^{h} \Pi_1(x_3) \, dx_3 = 0$$

(44)

Therefore, in order to achieve pumping one has to break the symmetry in $x_3$ direction.

Asymmetric Boundaries. We consider the limiting case of a channel with a hydrophilic bottom surface ($b_- = 0$) and a hydrophobic top surface ($b_+ \to \infty$). For symmetric spin slip conditions $s_- = s_+ = s$ we find from eq 36

$$\Pi_1 = \Theta \left( \frac{(x_3 + h)k \cosh kh - \sinh kh - \sinh kx_3}{2k(cosh kh + (1 + \eta_s / \eta) \cosh kh)} \right)$$

(45)

which for $\eta_s \ll \eta$ reduces to

$$\Pi_1 = \Theta \left( \frac{(x_3 + h)k \cosh kh - \sinh kh - \sinh kx_3}{2k \cosh kh + \cosh kh} \right)$$

(46)

For reasons already mentioned, and because again $s$ does not affect the shape of the flow profile, we set $s = 0$, leading to

$$\Pi_1 = \Theta \left( \frac{x_3 + h \cosh kh + \cosh kx_3}{2k \cosh kh} \right)$$

(47)

The profile of eq 47 is shown in parts e and f of Figure 2 as solid lines. In the asymmetric case, the integrated flow of the channel is for large channels ($kh \gg 1$) given by

$$\Phi = \int_{-h}^{h} \Pi_1 \, dx_3 = \Theta h^2$$

(48)

and thus $\Phi$ is clearly finite. It follows by comparison with simple shear flow that $\Theta$ is a measure of the shear rate in the channel.

Numerical Solution. To verify the validity of the assumptions inherent to the perturbative approximation, we solve eq 16 with eq 33 for the spin field and eq 15 for the velocity field numerically, subject to the boundary conditions of eqs 37 and 38. As input, the polarizability per mass $\alpha$ and relaxation time $\tau$ are needed, as well as the interfacial orienting dipole field $E_0$. To obtain those parameters we perform a series of molecular dynamics simulations.

Relaxational Parameters. We simulate a box of 2180 SPC/E water molecules ($4.0 \times 4.0 \times 4.0$ nm, isotropic pressure coupling, periodic boundary conditions in all directions) with an initially isotropic distribution of water dipoles. At $t = 0$, we turn on an electric field in the $x_3$ direction of strength $E_0 = 0.1 \text{ V nm}^{-1}$. Relative to experimental values, this is a strong electric field, but it is verified that the response is still reasonably linear. We perform 10 cycles of orientation (field turned on for 25 ps) and relaxation (field turned off for 25 ps), and average the result of the orientation part of each cycle. In Figure 3, we plot the average dipole moment per water molecule as a function of time. With a molecular dipole moment of SPC/E water of $\mu_{\text{SPC/E}} = 0.05 \text{ nm} e$, we see that the dipolar orientation is sufficiently far from being

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**Figure 2.** Rescaled flow velocity in channels of rescaled height $kh = 3$ (left) and $kh = 30$ (right) for vanishing spin slip length $s = 0$. Solid lines depict the flow profiles from the perturbative approach: (a and b) a symmetric hydrophilic channel (eq 42); (c and d) a symmetric hydrophobic channel (eq 43); (e and f) a channel with a hydrophilic bottom and hydrophobic top surface (eq 47). The numerical solutions to eqs 15, 16 and 33 are shown as dashed lines, using the interfacial dipolar orientation field $E_0^0(x_3)$ from simulations as input.


Figure 3. Average dipole moment per molecule, \(m_d \mu_I\), with \(m_0\) the mass of a water molecule, as a function of time after turning on an electric field of 0.1 V nm\(^{-1}\) (solid line). Shown as a dashed line is a fit with eq 49. In the inset, the applied electric field is shown.

saturated and we are thus in the linear-response regime. With \(\tilde{E} = E_3 \mu_1\) and \(\mu_1 = 0\) at \(t = 0\), the solution to eq 20 is

\[
\mu_1 = a(1 - e^{-t/\tau})
\]

Fitting eq 49 to the curve in Figure 3 gives a dipolar relaxation time of \(\tau = 7 \pm 2\) ps and a polarizability per unit mass of \(\alpha = 3.3 \pm 0.3 \times 10^6 m^2 eV^{-1}kg^{-1}\), with \(e\) the elementary charge. The value for \(\tau\) agrees within 20% with experimental numbers,\(^{37}\) and the value for the polarizability gives in conjunction with the Kirkwood–Fröhlich formula, \(\varepsilon = 1 + \rho \sigma / e_0\) with \(\rho = 10^3\) kg m\(^{-3}\), a value for the dielectric constant of \(\varepsilon = 61 \pm 6\), which is quite close to the known result of \(\varepsilon = 71\) for the SPC/E water model.\(^{38}\) The small deviation might be caused by nonlinear effects at the field strength used.

**Interfacial Orienting Dipole Field.** We also calculate the intrinsic orienting field \(E_3(x_3)\) from molecular dynamics simulations. We simulate two different systems, a hydrogen-terminated diamond and a hydroxide-terminated diamond, as a typical hydrophobic and hydrophilic system, respectively. The hydroxide-terminated surface is constructed by replacing every second C–H group at the surface of the diamond by a C–O–H group, representing a surface coverage of \(x_{OH} = 1/2\), in the notation of ref 39. The systems are solvated in a box of dimensions 6 \(\times\) 3 \(\times\) 5 nm containing 1856 SPC/E water molecules, and the electric field is calculated from integrating the charge density over the normal coordinate \(x_3\), assuming a relative dielectric constant of \(\varepsilon = 71\), which is the literature value for SPC/E water.\(^{38}\) In Figure 4, the resulting profiles of \(E_3\) for the two diamond surfaces are shown as a function of \(x_3\).

**Other Parameters.** The parameters used in the comparison are \(\eta = 10^{-3}\) Pa s, \(\eta_0 = 0.1\eta\),\(^{35}\) \(\rho = 10^3\) kg m\(^{-3}\), and \(\kappa^2 = 4\pi \eta_0 / [\sigma (\varepsilon + \eta_0)]\). For the spin viscosity, of which no estimates are available for water, we make the assumption \(\nu = a^2 \eta_0\) with \(a = 0.3\) nm of the order of the water molecule diameter. This assumption seems reasonable as it is very well obeyed by, e.g., liquid nitrogen.\(^{36,40,41}\)

As an example, we choose \(s_c = s_f = 0.5\) nm and \(b_- = b_+ = 1.5\) nm, which are reasonable values for a hydrophobic surface.\(^{39}\) As a dashed line in Figure 5a, the torque density \(\Gamma_3(x_3)\) obtained from eq 33 is shown as a function of \(x_3\), resulting from a rotating electric field and the \(E_3\)-profile of the hydrophobic diamond, shown in Figure 4b. The perturbative approximation of the torque density according to eq 34 is represented by a solid line. Clearly, the variations in the numerically calculated torque density, which are due to the dipole field \(E_3\) and the nonlinearity of eq 33, are small compared to the mean value, and the agreement with the perturbative result is very good. In parts b and c of Figure 5, the numerical solutions of eqs 15, 16, and 33 for the spin and velocity field are shown as dashed lines. The perturbative approximations of eqs 34, 35, and 36 for the torque density, spin field and the velocity field (solid lines in Figure 5) are in excellent agreement with the numerically calculated profiles, justifying the approximation for small electric field. For the boundary conditions \(b_- = 0, b_+ \rightarrow \infty\) and \(b_- = 0, b_+ \rightarrow \infty\), the numerical solutions are shown as dashed lines in the left panels of Figure 2, again showing good agreement with the analytically calculated profiles. Here we employ for \(E_3(x_3)\) the simulation results obtained with the hydrophilic diamond surfaces for the surfaces with \(b = 0\), and the simulation results obtained with the hydrophobic diamond surfaces for the surfaces with \(b \rightarrow \infty\).

**Power Dissipation.** For a rotating electric field we calculate the power dissipation per unit volume of fluid directly from the rotating dipole moment, leading to the average power dissipation of

\[
\mathcal{P} = \frac{\gamma}{2\pi} \int_0^{2\pi} \frac{\mathcal{F}^2}{\mathcal{F}^2} \frac{d\mathcal{F}}{dt} dt
\]


\(41\) Evans, D. J.; Streett, W. B. Mol. Phys. 1978, 36, 161.

**Figure 4. Electric field due to the dipolar ordering \(E_3\) as a function of \(x_3\) for (a) a hydrophilic diamond and (b) a hydrophobic diamond.**
Inserting the expressions for $\bar{u}$ from eq 31 and discarding terms of $\mathcal{O}(E^3)$, we obtain the explicit solution

$$P = \eta \gamma \Theta$$  \hspace{1cm} (51)

At the typical microwave oven driving frequency of $\gamma = 2\pi \times 2.5$ GHz and an electric field strength of $E_p = 10^{-4}$ V · nm$^{-1}$ we find $P = 9$ GW · m$^{-3}$. A similar calculation for a unidirectional oscillating electric field, on the other hand, yields $P_{\text{rad}} = \eta \gamma \Theta/2$, which is the standard expression for the dissipation due to dipolar relaxation given for example in ref 37. We thus see that rotating and planar electric fields exhibit identical dissipation, the factor 2 coming from the difference in the spatially averaged quadratic field strength.

Heating Effects. The channel height $2h$ at which the temperature difference between the center and the wall of the channel has a value $\Delta T$ is calculated from equating the heat transport through a surface area $A$ to the power dissipated in a volume $hA$,

$$kA \frac{\Delta T}{h} = P h A$$  \hspace{1cm} (52)

with $k$ the heat transport coefficient, which has the value $k = 0.6$ W · m$^{-1}$ · K$^{-1}$ for water. At $\gamma = 2\pi \times 2.5$ GHz and $E_p = 10^{-4}$ V · nm$^{-1}$, the height of the channel for which the temperature difference has the value $\Delta T = 10$ K follows from eq 52 as $h = 0.03$ mm. This directly shows that heating of the fluid due to dipolar dissipation is negligible for nanofluidic applications. For larger devices, heating can be reduced further by reducing the driving frequency or the electric field strength.

Pumping Efficiency. As a measure of the efficiency of electrohydraulic pumping with a rotating electric field, we compare the dissipation $P$ from eq 51 to the power dissipation of a simple shear flow generated by a force $F_0 \bar{u}_1$ acting on the top surface and a force $-F_0 \bar{u}_1$ acting on the bottom surface. We set the shear rate, which equals $u'_1 = F_0/\eta$, equal to $\Theta/2$ in order to match the shear generated in the rotating electric field case. The power dissipated per unit volume turns out to be

$$P_{\text{shear}} = 2F_0 u'_1 = \eta \Theta^2/2$$  \hspace{1cm} (53)

The dissipation ratio is given by

$$P_{\text{shear}}/P = \Theta/2\gamma \ll 1$$  \hspace{1cm} (54)

where for the last inequality we assumed that the response frequency $\Theta$ is typically much smaller than the driving frequency $\gamma$. It transpires that generating shear flows by exerting surface forces is for typical parameters more efficient than using a rotating microwave. Nevertheless, a microwave driven pump might be advantageous for other reasons in certain devices and applications.

Length Scales. In the limit of $\eta \ll \eta$, we find a spin screening length $\kappa^{-1} = 0.15$ nm, using the molecular length scale $a = 0.3$ nm. Conventional devices used to create a shear flow can be easily constructed down to a channel size of several tens of micrometers. The length scale $\kappa^{-1} = 0.15$ nm shows that the limit $kh \gg 1$ is relevant and realized already for nanometer-sized channels. A rotating electric field is therefore useful for creating shear flows in channels of a few nanometer up to tens of micrometers, where conventional devices are difficult to use and dipolar heating is not problematic yet. In the limit $kh \gg 1$, the profiles in the planar channels converge to a simple shear flow, with a shear rate of $\Theta/2$. Although the maximum shear rate is obtained for $\gamma \tau = 1$, let us consider the experimentally easily realizable driving frequency of $\gamma = 2\pi \times 2.5$ GHz, which is the driving frequency of a common microwave oven. For a realistic external field strength $E_p = 10^{-4}$ V · nm$^{-1}$, water viscosity $\eta = 10^{-3}$ Pa · s and density $\rho = 10^3$ kg · m$^{-3}$ we find a response frequency of $\Theta = 570$ s$^{-1}$ and thus predict sizable shear effects.

Cylindrical Geometry. We take $x_3$ to be the axial coordinate, $x_2$ the angular coordinate and $x_1$ the radial coordinate, see Figure 1b. Note that this is an uneven permutation of the usual form of the cylindrical coordinates. Again, we assume $\bar{u} = e_i \bar{u}_i(x_3)$ (axial flow) and $\bar{\omega} = \bar{\omega}_i(x_3)$ (only dependent on the radial coordinate). The Navier–Stokes equation in the $x_1$ direction transforms to

$$\frac{\rho \partial u_1}{\partial t} = \eta \left( \frac{\partial u_1}{\partial x_3} - 2\eta \omega_2 \right) + \frac{\nu}{\partial x_3} \left( \frac{\partial u_2}{\partial x_3} \right)$$  \hspace{1cm} (55)

Integrating eq 55 once over $x_3$ yields in the stationary state

$$0 = (\eta + \eta \gamma \partial u_1 / \partial x_3 - 2\eta \omega_2) - c_1 (\eta + \eta \gamma) / x_3$$  \hspace{1cm} (56)

At the same time

$$\rho \gamma \frac{\partial \omega_2}{\partial t} = \rho \Gamma_2 + 2\eta \gamma \frac{\partial u_1}{\partial x_3} - 2\eta \omega_2 + \frac{\nu}{\partial x_3} \left( \frac{\partial \omega_2}{\partial x_3} \right)$$  \hspace{1cm} (57)

Combining eqs 56 and 57 gives the cylindrical equivalent of eq 16

$$0 = \rho \Gamma_2 + (\nabla_3^2 - k^2) \omega_2 + \frac{2c_1 \eta \gamma}{\nu x_3}$$  \hspace{1cm} (58)

with $\nabla_3^2 = x_3^{-1}(\partial / \partial x_3)(x_3 \partial / \partial x_3)$. Static Electric Field. The torque resulting from a static electric field is given again by eq 22. In analogy to the planar case, a static field does not induce a flow through the nanotube.

Constant Torque. A steady state torque, on the other hand, will induce a flow in the cylindrical geometry. Equivalent to the planar case, the torque resulting from a rotating electric field is in good approximation a constant given by eq 34. Different from the planar situation, however, eq 38 with constant $\Gamma_2$ does not have an analytical solution. Therefore, we solve eq 38 numerically, after which the velocity profile is calculated from integrating eq 56. The geometry needed to generate an electric field rotating in the $x_1 - x_3$ plane consists of two concentric cylinders with radii $R_1$ and $R_2$, with the radius of the inner cylinder $R_1 > 0$ because eq 58 diverges for $x_3 = 0$. A rotating field is generated by applying a sine-like potential difference between the inner cylinder and the outer cylinder, and a cosine-like potential difference between two additional electrodes at both ends of the tube. The boundary conditions at $x_3 = R_1$, $R_2$ are given by the equivalent expressions of eqs 37 and 38. Due to the intrinsic asymmetry of the system in the $x_3$ direction, the velocity profile not only depends on the difference $R_2 - R_1$, but also on the absolute value of $R_1$. For $R_1 \to \infty$, eq 58 approaches eq 16, so we only treat the case for small $R_1$ here. In Figure 6, the numerically calculated flow profile is shown for two different values of the rescaled distance $x(R_2 - R_1)$ between the two concentric cylinders. The case of symmetric hydrophilic boundary conditions, $h_+ = h_- = 0$, is shown in Figure 6, parts a and b. Contrary to the planar case, the net flow $\Phi$ as defined in eq 44 is nonzero due to the asymmetry of the geometry in the $x_3$ direction. In parts c and d of Figure 6, the flow

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profile is shown for symmetric hydrophobic boundaries, $b_z = 0$, $b_z \rightarrow \infty$. In this case the net flow is zero because no momentum can be transferred between the tubes and the fluid. Finally, in parts $e$ and $f$ of Figure 6, the profile is shown for a hydrophilic inner cylinder and a hydrophobic outer cylinder, showing a net positive flow.

**Simulations**

**Interaction Energy.** In molecular dynamics simulations, the Lennard-Jones force is typically truncated at a finite cutoff distance, which can be done in various ways. The default way is to keep the force unchanged out to $r_c$ where the force is set to zero, leaving a force discontinuity at $r = r_c$. We will refer to this method as the simple cutoff scheme. Another way is to attenuate the force smoothly to reach zero at $r_c$ without discontinuity. In GROMACS, this so-called shifted force $F_s$ is implemented by adding a nonlinear function to the original force $F_o$:

$$F_s = \begin{cases} F_o + a r^2 + b r^3 & \text{if } r < r_c \\ 0 & \text{if } r \geq r_c \end{cases}$$

(59)

The coefficients $a$ and $b$ equal

$$a = -768 \epsilon \sigma^{12} r_c^{-15} + 240 \epsilon \sigma^6 r_c^{-9}$$

$$b = 720 \epsilon \sigma^{12} r_c^{-16} - 216 \epsilon \sigma^6 r_c^{-10}$$

(60)

with $\epsilon$ and $\sigma$ the parameters of the Lennard-Jones interaction and $r_c$ the truncation length in nanometers. The original Lennard-Jones force is given by

$$F_o = 4 \epsilon \left( \frac{1}{r^{12}} - \frac{1}{r^6} \right)$$

(61)

The interactions between dissimilar atoms are calculated by

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$$

and

$$\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$$

with indices $i$ and $j$ denoting the atom type. Examples of the simple and the shifted force are plotted in Figure 7. The curves have been verified by running simulations of two colliding particles.

**Other Simulation Details.** The long-range electrostatics are handled using particle mesh Ewald summation. For the simple cutoff scheme, the real-space truncation length for both the Coulomb interaction and the Lennard-Jones interaction is set equal to the list radius, which is the default option in GROMACS. For the simple cutoff scheme, setting the list radius larger than the truncation length is not allowed in GROMACS. For the shifted scheme, the real-space truncation length for the Coulomb interaction and the list radius is set 0.2 nm larger than the Lennard-Jones interaction. The temperature is kept constant at 300 K using a Berendsen thermostat. All systems are equilibrated at a constant pressure of 1 bar using a Berendsen barostat. After which the substrate is frozen and the simulation is run at constant volume, except for the nanotube simulations with reservoir, where an anisotropic Parrinello–Rahman barostat is used throughout the whole simulation. We use periodic boundary conditions in all directions.

We perform molecular dynamics simulations for both Lennard-Jones truncation schemes and for different values of $r_c$:

- It is verified that the update frequency of the list of interacting atoms has no influence on the velocity of the molecules.
- For the simple cutoff scheme, choosing a list radius smaller than the truncation length is found to make no difference.
Running simulations using single (32 bits) or double (64 bits) numerical precision give the same results.

Changing the real space Coulomb truncation length does not make any difference, as expected.

Choosing the list radius and real-space Coulomb cutoff length equal to the Lennard-Jones truncation length in the shifted scheme does not change the results.

Using a Nosé–Hoover thermostat instead of a Berendsen thermostat does not change the velocity of the molecules.

We simulate three different planar substrates in pure water. The first simulation system consists of a hydrogen-terminated diamond surface (double FCC, 2323 C-atoms, 226 H-atoms), solvated in 920 water molecules, giving a total system size of \(3.2 \times 3.2 \times 4.7\) nm. The carbon atoms are modeled by the GROMOS 96 force field \((\epsilon = 0.277\ \text{kJ mol}^{-1}, \sigma = 0.358\ \text{nm})\), where \(\epsilon\) and \(\sigma\) refer to the interaction between similar atoms. The hydrogen atoms have their usual mass, but the Lennard-Jones parameters are set to zero. The contact angle of the diamond equals \(\sim 111^\circ\), as calculated from the virial tensor. \(^{44}\)

A second set of simulations are performed for an oil slab solvated in water. The simulation box has a size of \(4.0 \times 4.0 \times 5.9\) nm, containing 250 CH\(_3\)(CH\(_2\))\(_5\)CH\(_3\) (heptane) molecules and 1013 water molecules. The heptane is modeled exactly as in ref 24, with five unified CH\(_2\) atoms (Lennard-Jones parameters: \(\epsilon = 0.411\ \text{kJ mol}^{-1}, \sigma = 0.407\ \text{nm}\)) terminated with 2 CH\(_3\) atoms (Lennard-Jones parameters: \(\epsilon = 0.867\ \text{kJ mol}^{-1}, \sigma = 0.375\ \text{nm}\)). The third simulation system consists of two frozen sheets of graphene, separated by a vacuum gap of 2.5 nm. The Lennard-Jones parameters of the carbon atoms are identical to the ones used for the diamond simulations. The system is solvated in 1339 water molecules, giving a system size of \(4.3 \times 4.4 \times 4.9\) nm. All simulation systems are visualized in Figure 8.

We also simulate an artificial hydrophobic surface identical to the one used in ref. 5, solvated in 1 M sodium chloride. The surface consists of an FCC lattice of atoms with Lennard-Jones parameters \(\epsilon = 0.686\ \text{kJ mol}^{-1}\) and \(\sigma = 0.337\ \text{nm}\) and has a contact angle of \(140^\circ\). The Lennard-Jones parameters of the ions are given by \(\epsilon = 0.0617\ \text{kJ mol}^{-1}\) and \(\sigma = 0.258\ \text{nm}\) for Na\(^+\) and \(\epsilon = 0.446\ \text{kJ mol}^{-1}\) and \(\sigma = 0.445\ \text{nm}\) for Cl\(^-\). The interplate distance corresponds to a pressure of 10 ± 5 bar. \(^4\)

For the cylindrical geometry we simulate three nanotubes (CNT’s): a (10,0), a (16,0) and a (16,16) CNT, with diameters of 0.782, 1.25, and 2.17 nm respectively, as shown in Figure 9. The tubes have a length of 10, 10, and 5 nm, containing 37, 202, and 358 water molecules respectively. The C–C bond has a length of 0.142 nm and the Lennard-Jones parameters of the carbon atoms are identical to the ones used for the diamond simulations. The CNT’s are equilibrated in a large bath of solvent using a semi-isotropic Berendsen barostat at 1 bar. After equilibration, the water outside the nanotube is removed. In axial direction, the simulation box is set to the same size as the nanotube, so the nanotube is connected directly to its periodic image. In the other two directions, the box size is \(5 \times 5\) nm. In a different setup, we simulate a (16,0) CNT that connects two water reservoirs (see Figure 10), to compare our results quantitatively to the results of

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ref 25. The total size of the periodically repeated reservoir is 4.0 \times 3.6 \times 1.8 \text{ nm}. There are 1057 water molecules in the system.

Flow Profiles. Planar Geometry. First, we present simulation results for the diamond surface with a simple cutoff scheme at \( r_{c} = 0.8 \text{ nm}. \) The water density between two periodic images of the diamond is shown in Figure 11a. We define the bulk of the system as the region where the water density is constant. The velocity of the fluid is calculated from a numerical derivative of the positions of the centers of mass of the molecules. In Figure 11b, the velocity profile of the water, \( u_{1}(x_{3}) \), is shown. The velocity in the \( x_{1} \) direction is clearly nonzero, and the fluid moves in the direction of the external electric field, in marked contrast to the analytical results presented in the previous sections. We will clarify this contradiction further below. As a dashed line in Figure 11c, the \( x_{2} \)-component of the vorticity \( \nabla \times u_{1} \) is shown, together with the spin field \( \omega_{2} \) depicted with a solid line. According to eq 15 the vorticity should be a linear function of the spin field. Although the vorticity is nonzero, the spin field is zero over the whole range, indicating an unphysical decoupling of the spin and vorticity, which might serve as a first hint to the failure of the simulation method.

Cylindrical Geometry. In Figure 12a, we plot the density inside a (16,16) CNT using a simple cutoff scheme at \( r_{c} = 0.8 \text{ nm}. \) Inside the carbon nanotube, the density never reaches a constant value. Since the velocity shows a plug profile (Figure 12b), we calculate the average velocity of all water molecules inside the tube and use it for further analysis. In Figure 12c, the spin field \( \omega_{2} \) is shown as a function of \( x_{3} \). The noise near the nanotube wall and in the center is due to bad statistics, caused by molecules entering the depletion layer for a very short time near the wall and by the small averaging volume in the center. In between the center and the surface, the spin field is zero like in the planar case.

Truncation Length Dependence. Rectangular Geometry. No Ions. In Figure 13, the \( \zeta \)-potential of the three planar substrates is shown for the two different truncation schemes. The \( \zeta \)-potential is calculated from eq 1, and the error bars depict the statistical standard deviation of the velocity in the bulk region as defined above. Clearly, the \( \zeta \)-potential of all three substrates depends strongly on the truncation scheme used. This dependence on the truncation scheme has no physical meaning, since the minute change of the force profile should not lead to such a tremendous variation of the flow velocity. Besides, according to our analytic calculation, the flow must vanish irrespective of
details of the force. The unphysical dependence on the cutoff length in the simple truncation scheme vanishes for large values of the truncation length, and the $\zeta$-potentials in both cutoff schemes converge to zero. The truncation length dependence of the $\zeta$-potential shows that the nonzero flow observed in Figures 11b and 12b and by refs. 24,25 is an artifact related to the implementation of the Lennard-Jones force truncation in the simple cutoff scheme.

**Nanotubes without Reservoir.** The $\zeta$-potential of the nanotubes is calculated from the average velocity inside the tube using eq 1. In Figure 14, we plot the $\zeta$-potential of the three nanotubes as a function of the truncation length, showing the same convergence to zero electro-osmotic flow as in the rectangular cases. This zero-flow result is in agreement with our analytical theory for the cylindrical geometry. Comparison of our results for the planar and cylindrical cases show that the spurious flow effect is obtained irrespective of details of the geometry.

**Nanotubes with Reservoir.** To estimate the $\zeta$-potential of the (16,0) CNT connecting two reservoirs, we calculate the flux in $x_1$ direction through a cross section located at one end of the nanotube. Note that our definition of the flux differs from the definition used in ref. 25. The average velocity $u_i$ inside the nanotube is calculated by dividing the flux by the linear molecule density inside the nanotube, after which the $\zeta$-potential is calculated from eq 1. The resulting $\zeta$-potential is shown in Figure 15 as a function of the truncation length. Like in the case without reservoir, the $\zeta$-potential depends on the Lennard-Jones truncation scheme and on the truncation length used. However, the $\zeta$-potential in the geometry with reservoir is significantly lower than in the case without reservoir, indicating that the reservoir strongly hinders the spurious transport.

**Rectangular Geometry, with Ions.** In Figure 16, we show the result of simulations performed with exactly the same simulation box as Huang et al. use.2,5 The liquid in these simulations is a 1 M electrolyte solution of sodium chloride. Huang et al. use a simple cutoff scheme with a truncation length of 1.0 nm and the LAMMPS simulation package, giving zero electro-osmotic flow.

The fact that our simulations yield a nonzero $\zeta$-potential using a simple cutoff scheme indicates that this is a GROMACS related issue and not due to the simple cutoff per se. Note that in simulations of electrolyte solutions at neutral surfaces, in principle a small but finite electrokinetic effect can in principle exist because the sodium and chloride ions have slightly dissimilar surface affinities giving rise to a small electrostatic surface potential. But this small contribution is totally dominated by the erroneous flow generated within the simple cutoff scheme.

**Conclusion**

Using a combination of analytical theory based on a generalized Navier–Stokes equation and molecular dynamics simulations, we show that interfacial water ordering does not give rise to steady state flow in static electric fields. This means that the interfacial dipole potential due to the water ordering does not contribute to the $\zeta$-potential. Nevertheless, electro-hydraulic pumping of dipolar fluids is possible: an electric field step function gives rise to transient flow, while a rotating electric field in an asymmetric channel can be used to drive flows in steady state. In a symmetric channel, a rotating electric field induces a shear profile but no net pumping. The equilibrium flow observed with static electric fields in previous molecular dynamics simulations of pure water were caused by particularities of the simple Lennard-Jones force truncation scheme in GROMACS. The unphysical dependence of the flow velocity on the Lennard-Jones truncation scheme vanishes for infinite cutoff length $r_c \to \infty$ for all simulated geometries and surfaces. Using a shifted Lennard-Jones truncation scheme within GROMACS, pure water does not give rise to a nonzero $\zeta$-potential for any value of the truncation length, in agreement with the analytical theory presented. Using the LAMMPS molecular dynamics package, the spurious flow effect is not observed, regardless of the truncation scheme used.5

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**Figure 14.** $\zeta$-potential calculated from the average velocity inside (a) (10,0) CNT, (b) (16,0) CNT, and (c) (16,16) CNT, without reservoir, as a function of the truncation length $r_c$.

**Figure 15.** $\zeta$-Potential of a (16,0) CNT between two reservoirs as a function of truncation length $r_c$.

**Figure 16.** $\zeta$-Potential of an artificial hydrophobic surface (consisting of an FCC lattice of Lennard-Jones atoms) in the presence of a 1 M sodium chloride solution as a function of the truncation length $r_c$.