Osmotic traps for colloids and macromolecules based on logarithmic sensing in salt taxis†

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Diffusiophoretic motion of colloids and macromolecules under salt gradients exhibits a logarithmic-sensing, i.e. the particle velocity is proportional to the spatial gradient of the logarithm of the salt concentration, as \( V_{DP} = D_{DP} \nabla \log c \). Here we explore experimentally the implications of this log-sensing behavior, on the basis of a hydrogel microfluidic device allowing to build spatially and temporally controlled gradients. We first demonstrate that the non-linearity of the salt-taxis leads to a trapping of particles under concentration gradient oscillations via a rectification of the motion. As an alternative, we make use of the high sensitivity of diffusiophoretic migration to vanishing salt concentration due to the log-sensing: in a counter-intuitive way, a vanishing gradient can lead to measurable velocity. As an alternative, we make use of the high sensitivity of diffusiophoretic migration to vanishing salt concentration due to the log-sensing: in a counter-intuitive way, a vanishing gradient can lead to measurable velocity.

At equilibrium, small particles like colloids and macromolecules are subjected to thermal Brownian motion, leading to an unavoidable diffusive exploration of their spatial environment. On the other hand, it is possible to overcome Brownian motion and induce directed motion of colloids under the application of gradients of thermodynamic variables. Classical examples involve electro-phoresis—transport under an applied electric field—, thermophoresis—transport under a temperature gradient—, and diffusiophoresis—transport under a solute gradient—, as well as variations of these phenomena, such as dielectrophoresis or induced charge electrophoresis. These phenomena have been extensively studied over the years, but new opportunities were offered by recent experimental developments in microfluidic technologies, which have led to some important new ways to separate, concentrate or screen particles.

In this paper, we focus on the formation of patterns of colloidal population, which originate in the non-linear behavior of diffusiophoretic (DP) transport. Diffusiophoresis is the osmotically induced motion of particles— colloids or macromolecules—under a gradient of solute, here salts. We show that under certain conditions, this phoretic directed motion may be used to create osmotic colloidal traps of various geometries, thereby overcoming Brownian motion to confine the particles. We will follow two different strategies, both of which rely upon the non-linearities of DP motion as a function of salt concentration: (i) traps created by the rectification of time-dependent salt gradients; (ii) traps created by an ‘osmotic’ shock resulting from a step change of the salt concentration at the boundaries. These various phenomena are rationalized on the basis of a theoretical description for the time-dependent Smoluchowski equation for the colloidal density.

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Diffusiophoresis is an interfacially driven transport phenomenon. It results from an unbalanced osmotic pressure gradient occurring within the diffuse layer in the close vicinity of the solid (typically of the order of a few nanometres), this interface thereby playing the role of the semi-permeable membrane in classical osmosis. This induces an interfacial flow along the surface leading to the motion of the colloidal particle in the surrounding medium. While this mechanism has been known for some time, it was recently re-investigated experimentally, by using the benefits of microfluidics technology to study the diffusiophoretic migration of particles in well-defined solute gradients.

In ref. 3, 12, diffusiophoresis under small salt contrasts was e.g. shown to boost a diffusive-like migration of colloidal particles in a co-flow geometry. For salts as a solute, the DP velocity of particles is expected to exhibit a log-sensing migration, in the form:

\[
V_{DP} = D_{DP} \nabla \log c.
\] (1)

This log dependence originates in the specific electrostatic interaction between the ionic salt solute and the charged surface. Such a behavior was shown to be in quantitative
agreement with the observations in ref. 3,12. In principle, the
diffusiophoretic mobility $D_{DP}$ may depend on salinity, via the
ionic force dependence of the zeta potential. A logarithmic
dependence of the zeta potential versus salt concentration—and
thus of $D_{DP}$—is indeed usually reported in the low salinity
regime.21 In the following, we shall neglect this weak dependence of $D_{DP}$ with the salt concentration, which is expected to play only
a minor role in the diffusiophoretic dynamics of colloids.

In this paper, we explore the consequences of this logarithmic
sensing. Indeed, log-sensing does present very interesting features: (i) a non-linearity vs. salt concentration and (ii) an extreme sensitivity to vanishingly small salt concentration $c \to 0$.

As a side note, such a logarithmic sensing has been recently
reported in living systems for the chemotactic migration of E. Coli
bacteria.21 We will then explore two scenarios taking benefit of
these log-sensitivity features of DP migration to collect colloidal
particles in ‘osmotic traps’ against Brownian motion: (i) trapping
by rectification under oscillating solute gradient; and (ii) trapping
by an osmotic shock.

This paper is organized as follows. First we characterize the
DP migrations of particles—colloids or biological macromolecules—in a controlled electrolyte gradient without flow thanks to
a specifically designed hydrogel microfluidic device. Then we
show that the oscillation of salt gradients induces a trapping of
colloids by a rectification effect of the DP migration. Finally we
show that an abrupt change of salt concentration at the
boundaries of the system induces a strong trapping of the
colloids towards the center of the cell, a situation which we quote
as an osmotic shock. These various phenomena are rationalized
on the basis of a theoretical analysis of the time-dependent
Smoluchowski equation for the colloid density.

1 Diffusiophoresis in a controlled gradient

A detailed study of diffusiophoretic motion relies on the ability
of generating and controlling a concentration gradient of a solute.
Along the same lines as recent studies of bacterial chemotaxis,22,23 we have developed a microfluidic device made of
agarose hydrogel to build such concentration gradients. The
principle of the device is sketched in Fig. 1a and relies on the
porous nature of the hydrogel:24 the hydrogel matrix acts as solid
walls for the flow but allows the free diffusion of salt or small
molecules. A solute gradient is created across the system by
imposing two different concentrations through boundary channels: the source with concentration $c_1 = c_0$, and the sink with
$c_2 = 0$. This externally controls the solute gradient inside the
central microfluidic chamber containing the particles under
investigation (colloids or DNA) without any spurious flow.

The set-up, sketched in Fig. 1a, enables stationary as well as
temporally switchable solute gradients in various microfluidic
designs. The microfluidic design is made of two side channels
along microfluidic chambers of various sizes (typically 200–
600 µm) and shapes (rectangular or circular). Further experimental
details on hydrogel microfluidics are given in the
appendix, Materials, Preparation and Methods section. Globally,
a solute gradient, here either of fluorescein, or of a salt—LiCl, NaCl or KCl salts—is created in the central microfluidic chambers containing the particles via two side channels which impose
the concentration boundary conditions. The latter can be

![Fig. 1](image-url)

(a) Experimental Setup: a hydrogel microfluidic device. A double syringe pump with two solutions of salt of concentration $c_1$ and $c_2$ fills the two side channels. A microfluidic switch allows to exchange the salt solutions in the side channels, leading to a time-dependent tuning of the gradient. Particles under investigation (colloids and λ-DNA) are located in the center microfluidic chamber. (b) Calibration with fluorescein. Top view of the microfluidic device setup. The inner box shows the experimental fluorescence intensity image measured for the stationary gradient (gel walls not represented) of a fluorescein solution ($c_1 - c_2 = 10^{-4}$ M). The central chamber width is $w = 300$ µm while $l = 800$ µm is the total diffusion width (scale bar is 300 µm).

switched, on demand, thanks to a manual microfluidic switch
which inverts the side-channel’s solute concentration. The
dynamics of the concentration profile is given by the diffusion
equation:

$$D_s \Delta c = \delta_c$$

where $D_s$ is the salt diffusivity and the boundary conditions are
set by the concentration $c_1$ and $c_2$ in the two side channels.

At steady state, eqn (2) reduces to $\Delta c = 0$ and gives a linear
profile for the concentration in one dimension. We define the
length scale $l$ as the length over which the gradient develops, i.e.
the distance between the side channels and $x = 0$ in the middle
of the microfluidic chamber (see Fig. 1b, left). Given the boundary
conditions $c(-l/2) = c_1$ and $c(l/2) = c_2$, one can finally rewrite
the steady profile of the solute concentration:

$$c(x) = \frac{c_0}{2} \left(1 \pm 2\frac{x}{l}\right)$$

± depending whether the source is the side channel on ±/2.

For a 2D circular geometry, the solution is given by series of
Bessel functions as imposed by the boundary conditions
(see below).

1.1 Calibration of the gradient

The gradient profile is calibrated using a fluorescein solution
(Roth) of concentration $c_0 = 10^{-4}$ M. In this range of concen-
tration, Diao et al. showed a linear relation between the fluo-
rescein concentration and the fluorescence intensity24 making
the fluorescent measurement a straightforward visualization of the
chemical concentration field in the channel. A syringe pump fills
one side channel with a fluorescein solution $c_1 = 10^{-4}$ M (the
source) and the other with distilled water $c_2 = 0$ M (the sink).
A manual switch inverts the roles of source and sink and reverses the gradient. Measurements are performed for linear channels i.e. linear side channels and a rectangular microfluidic chamber as sketched in Fig. 1a.

Steady concentration gradient. The steady concentration gradient is linear (see Fig. 2a) in agreement with theoretical expectations. The profile can be reversed by actuation of the microfluidic switch (red and blue curves). We check experimentally that the solute flux in the source/sink is sufficient to define constant boundary conditions along the channel. In other terms, the Peclet number \( Pe = \frac{D_U}{\xi} \), which compares the diffusive time \( \tau_D = \frac{L^2}{D_f} \) for the boundary conditions to diffuse along the length scale \( L \) with the convective time \( \tau_C = L/U \) for the fluid to go from the inlet to the outlet, should be large, so that feeding in salt is assured. These conditions rewrite \( Pe = \frac{\xi^2 U}{D_f L} \gg 1 \), where \( L \approx 10 \) cm is the length of the side channels, \( U \approx 3 \) cm s\(^{-1}\) the velocity of the injected solutions, \( \xi \approx 800 \) \( \mu \)m and \( D_f = 420 \) \( \mu \)m\(^2\) s\(^{-1}\), the fluorescein diffusion coefficient.\(^\text{25}\) Under the present conditions, the Peclet number is of the order \( Pe \approx 450 \) and is much larger than unity. This ensures the steadiness of the boundary conditions both during the calibration step with fluorescein and the experiment as LiCl diffuses faster than the fluorescent salt (for LiCl \( D_s = 1360 \) \( \mu \)m\(^2\) s\(^{-1}\), corresponding to a Peclet number \( Pe = \xi U/D_f \approx 140 \)).

Transient concentration gradient. Following the reversal of the side boundary conditions, the concentration profile is in a transient state. The experimental visualization of the transient gradient is monitored with the temporal evolution of the difference \( \Delta c \) of the fluorescence intensity on both sides of the central chamber (see Fig. 2b). On this figure, steady and transient concentration profiles are visible. After a sharp increase during the transient state, \( \Delta c \) evolves slowly. The slow increase of \( \Delta c \) is attributed to the 3D diffusion of the fluorescent salt in the ‘ceiling’ of the microfluidic chamber. We measure a transient time \( \tau_T \approx 2 \) min for fluorescein and \( \xi = 800 \) \( \mu \)m. One can then estimate the transient time for LiCl salt, by rescaling the time measured for fluorescein by the ratio of the diffusion constant of fluorescein \( (D_f = 430 \) \( \mu \)m\(^2\) s\(^{-1}\)) to LiCl salt \( (D_s = 1360 \) \( \mu \)m\(^2\) s\(^{-1}\)):

\[
\tau_T \approx \frac{430}{1360} \times 2 \text{ min} \approx 35 \text{ s}
\]

Finally after a few tens of seconds for salts, we can assume a linear and steady concentration profile of salt in the microfluidic chamber containing the particles under investigation.

1.2 Diffusiophoretic migration

We now consider the situation where particles have been enclosed in the central chamber. We first concentrate on the case of latex colloids with a 200 nm diameter.

Qualitative approach. We start from a configuration where all particles are gathered on one side of the channel (see Fig. 3a at \( t = 0 \)). At \( t = 0 \) a salt gradient with high concentration of salt opposing the position of the colloids is imposed. The colloids are observed to exhibit a purely transverse motion under the imposed concentration gradient (see Fig. 3a). The drift is along the salt concentration gradient and towards the higher solute concentration thus revealing a diffusiophoretic migration of the colloids under the salt gradient (see Fig. 3a). The diffusiophoretic velocity is typically 1 \( \mu \)m s\(^{-1}\). When particles have gathered at the opposite wall, the gradient is reversed again thus showing a symmetrical behavior with a reversed transverse motion (see ESI,§ movie 1).

Analysis of the experiment. In order to quantify the diffusiophoretic motion, we plot in Fig. 4a the time dependent location of the colloid population. It is defined as the maximum \( X_0 \) of the fluorescence intensity profile measured using image analysis (see appendix, Materials, Preparation and Methods section). As can be seen, the observed drift is close to linear with

Fig. 2 (a) Steady fluorescence intensity profiles: a linear concentration gradient. Temporal changes in boundary conditions upon actuation of the microfluidic switch lead to gradient inversion (red and blue curves). (b) Temporal evolution of the gradient—for periodic actuation \( T_0 = 10 \) mins—of the difference \( \Delta c \) of fluorescence intensity on both sides of the central chamber following a gradient inversion.

Fig. 3 Diffusiophoretic transport of (a) fluorescent colloids and (b) \( \lambda \)-DNA under a LiCl gradient. (Linear geometry with \( \xi = 800 \) \( \mu \)m, scale bar 100 \( \mu \)m). (a),(b) Motion of the particles under a salt gradient, sketched by the lateral bar, towards higher salt concentrations. Images are separated by 90 s for the colloids and for DNA the images were taken at \( t = 100, 150, 200, 300 \) s.
a slight deviation observed at long times. Neglecting the transient regime (lasting for ∼ 30 s for a salt, see section 1.1) over the crossing time in the experiment (typically ∼ 300 s) we consider only the stationary salt concentration profile:

\[ c(x) = \frac{c_0}{2} \left( 1 + \frac{2x}{l} \right), \]

see eqn (3) (± depending on the position of the source channel on ± l/2). Using the expression of the diffusiophoretic velocity \( V_{DP} = D_{DP} \frac{\nabla c}{c} \) (see eqn (1)) in a steady linear concentration (see eqn (3)), the position \( X_0 \) of a colloid obeys the equation:

\[
\frac{dX_0}{dt} = \pm D_{DP} \frac{1}{\left( \frac{l}{2} \pm X_0 \right)^2}.
\]

Initially, all colloids are concentrated at a position \( X_0(t = 0) = \mp w/2 \) where \( w \) denotes the width of the central channel. For short times \( dX_0/dt = \pm 2D_{DP}(l/\mp w) \) the maximum of the colloid density exhibits a quasi-linear dependence on time, as observed experimentally in Fig. 3b. For longer times, slight deviations from the linear dependence are expected from eqn (4) and are fully superimposed on the previous results. The black dashed line on (a) is a guide line corresponding to constant drift velocity. Shaded regions correspond to time periods where wall effects prevent from proper fluorescence measurements.

Taking the results for LiCl as a reference, this “integrated” method yields diffusio-phoretic mobilities \( D_{DP} \) in agreement with the values determined by the complete fit of \( X_d(t) \), as expected.

In the case of colloids, the diffusiophoretic mobility was measured for three different salts, exhibiting salt specificity effects with values for the mobility in the order LiCl > NaCl > KCl (see Table 1). This specificity stems from the difference of diffusivity between anions and cations of a given salt, which induces a corresponding electric field and an induced electrophoresis.\(^1,^3\)

### Diffusiophoretic migration of DNA macromolecules

As we now show, DP migration is not limited to spherical colloids as macromolecules also undergo DP motion. As a demonstration, the same motility experiments are conducted with phage-λ DNA (whose radius of gyration is typically 200 nm, see appendix, Materials, Preparation and Methods section) under a LiCl gradient. The salt gradients induce the migration of this macromolecule towards the high concentration of salt (see Fig. 3b). It demonstrates the motion of DNA molecules induced by an electrolyte gradient. The determination of the diffusiophoretic mobility of the DNA by the fitting method is more tedious as the experimental curve presents a much higher non-linearity for the velocity than predicted for simple colloids (see Fig. 4b). There is actually no firmly grounded theoretical prediction for DP transport of macromolecules like DNA and we use here the result for spherical colloids as a guideline. The quantitative disagreement observed with this prediction underlines that the basic derivation for spherical solid colloids does not fully capture the specificity of the dynamics of a complex macromolecule such as DNA. However, while further work is needed to theoretically describe the diffusiophoretic migration of DNA, the present experiments nevertheless confirm the migration of biological molecules towards high concentration of salt. As a final remark,

<table>
<thead>
<tr>
<th>Salt</th>
<th>Colloid</th>
<th>DNA</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>290 ± 5</td>
<td>150 ± 20</td>
</tr>
<tr>
<td>NaCl</td>
<td>150 ± 10</td>
<td>70 ± 10</td>
</tr>
<tr>
<td>KCl</td>
<td>70 ± 10</td>
<td>150 ± 20</td>
</tr>
</tbody>
</table>

\[ D_{DP} (\mu m^2/s) \]

\[ T_{cr}/T_{cr} = D_{DP}(\ell/w) \]

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we emphasize that while salt is used here, because of its simplicity, other solutes could be used as an alternative.1,16

Conclusions. To summarize at this stage, we have demonstrated experimentally that the diffusio-phoretic migration of colloidal particles in an electrolyte exhibits three main features: (i) motility driven by concentration gradient; (ii) salt specificity effects; and (iii) logarithmic-sensing \( i.e. V_{DP} = D_{DP} \log c \). This confirms two non trivial characteristics of the DP transport under a salt gradient: (i) it is non linear and (ii) the velocity becomes increasingly large at a vanishing solute concentration. In the following we use the benefits of these characteristics to obtain a versatile localization process of the particles.

2 Trapping by rectified diffusiophoresis

The diffusiophoretic motion of a colloidal particle in an electrolyte gradient is characterized by a logarithmic-sensing which introduces a slight non-linearity in the velocity to concentration relationship. This suggests that rectification of the particles motion should occur under periodic oscillations of the salt gradient. We explore this feature for particle trapping and patterning.

Interlude: time-scales in the experiment

The diffusiophoretic migration was studied in a steady gradient, we now generate concentration gradient oscillations as in Fig. 1b, c by periodic inversions of the concentration boundary conditions (half period \( T_{o/2} \)). This brings to three different time-scales in the experiment: the transient time \( T_{tr} \), the crossing time \( T_{c} \), formerly defined and the oscillation period \( T_{o} \). In this short paragraph we discuss how they are handled in the experiments.

Up to now we neglected—for the sake of simplicity—the transient state of the gradient and considered only the steady gradient. Diffusion in the hydrogel acts as a low-pass filter for the imposed boundary conditions which need time to diffuse. It thus constrains the half period \( T_{o/2} \) to be much larger than the transient time \( T_{tr} \). Furthermore \( T_{o/2} \) is taken to be much lower than the crossing time \( T_{c} \) to limit finite-size effects and accumulation of colloids blocked along the chamber walls. Finally, it leads to a compromise for the oscillation period: \( T_{o} \ll T_{o/2} \ll T_{tr} \). With a constant \( \ell = 800 \mu m \) in all experiments, the transient time is \( T_{tr} \approx 30–60 \) s (see section 1.2) and the crossing time \( T_{c} \approx 6–15 \) min. Given the experimental parameters—channel geometry and colloids samples—the oscillation period is the only experimentally tunable parameter. It is chosen in the range 6 to 10 min \( i.e. \) the time for colloids to cross typically 1/5 to 1/3 of the channel.

2.1 Osmotic trapping of colloids

As stated in the previous section, we chose \( T_{o} \approx 6–10 \) min depending on the salt and therefore on the crossing time. We start from a homogeneous concentrated population of colloids (F8888, 200 nm, Molecular Probes) in the central chamber.5

After each oscillation the population of colloids is depleted close to the wall of the channels and after 3–4 oscillations the colloids are trapped in the center of the channel. The period of oscillations is then reduced to prevent any contact with the chamber walls and ensure that trapping is not a consequence of a geometrical constraint. The band then keeps oscillating around the center with the salt cycles, but its width remains stationary. An experiment is shown in Fig. 5a) for colloids: starting from a homogeneous distribution, the particle population evolves after a few cycles towards a band with a stationary width. This band is Gaussian to a very good approximation (see Fig. 5a). The process is utterly robust: starting from an inhomogeneous particles distribution, or changing the oscillation frequency—within our limited accessible range as specified earlier—yields the same width for the trapped band. Finally, for the colloid motility, the width of the trapped band depends on the salt nature: LiCl > NaCl > KCl in terms of trapping efficiency.

Additionally, we perform similar experiments with \( \lambda \)-DNA as motile particles and show in Fig. 5b) that trapping is equally achieved with such biological colloids. They gather in a narrow band with Gaussian profile as well.

2.2 Principle in a nutshell

We now present a cartoon picture that captures the physics at work in the observed phenomenon of particle segregation with oscillating concentration gradients. We consider a syringe pump that contains a salt with a given concentration \( c_{o} \) while the other

![Fig. 5 Trapping under salt gradient oscillations.](attachment:image.png)

The concentration profile of the colloids inside the chamber is imaged by the spatial fluorescence intensity in the chamber with a 20× objective, see appendix Materials, preparation and methods section. The illumination is strongly attenuated by a microscope filter and shut off between pictures to limit bleaching of the colloids.

\footnote{The concentration profile of the colloids inside the chamber is imaged by the spatial fluorescence intensity in the chamber with a 20× objective, see appendix Materials, preparation and methods section. The illumination is strongly attenuated by a microscope filter and shut off between pictures to limit bleaching of the colloids.}
contains only buffer. For the sake of simplicity, we will first suppose that the linear steady profile of the gradient is reached instantaneously after a reversal of the boundary conditions i.e. we neglect the transient regime. Initially, we suppose that the high concentration of the salt is on the right side of the chamber: source on the right, sink on the left (see Fig. 6). A colloid initially on the left side on the chamber migrates to the right thanks to the diffusiophoresis phenomenon (see Fig. 6a). After a time $T_0/2$, the colloid has crossed a part of the chamber and the salt gradient is reversed. The colloid attracted by the high concentrations of salt reverses the direction of its motion and migrates to the left (see Fig. 6b). At time $T_0$, the concentration gradient is reversed and so on...

In other words, under a constant solute gradient, the velocity of particles is larger in regions with smaller solute concentration. Accordingly, the front particles move slower than the ones at the back and after one period and a complete oscillation of the boundary conditions, the colloid has experienced a net displacement towards the center of the chamber (see Fig. 6c). After a few oscillations, any colloid initially in the chamber ends up in the center $x = 0$. Iterated over the oscillations, such a process leads to the observed focusing, which is only limited by Brownian diffusion of the colloids. Altogether, this trap phenomenon takes its origin in the non-linear-sensing of the diffusiophoretic migration in electrolyte solutions (see eqn (1)).

### 2.3 Theoretical predictions

**Numerical simulations.** In order to get further insights into how the trapping mechanism works, we conduct a detailed investigation of the particles dynamics. The rectification is induced by the non-linear sensing of the diffusiophoretic motion, $V_{DP} = \nabla [\log c]$ (see eqn (1)) where $c(x,t)$ stands for the salt concentration field. Our starting point for the modelization is the Smoluchowski equation for the particles concentration, $\rho(x,t)$, here coupled to the salt diffusive dynamics:

$$
\begin{align*}
\partial_t \rho &= -\nabla \cdot ( - D_s \nabla \rho + D_{DP} \nabla [\log c] ) \\
\partial_t c &= D_s \Delta c
\end{align*}
$$

where $D_s$ is the particle diffusion constant, $D_s$ is the salt with concentration $c$ and $D_{DP}$ the particle diffusiophoretic mobility. These equations are coupled to the time-dependent boundary conditions for the salt concentration: every $T_0/2$, the salt concentration at the boundaries switches from 0 to $c_0$ for one side and vice versa for the other side. At time $t = 0$ the particle distribution is chosen homogeneous in most cases but various initial conditions were implemented and tested. The geometry fits that of the experiments, with particles confined in the central channel while the salt gradient develops over the central channel and the gel walls. Further details on the numerical resolution of the set of equations eqn (6) are given in the appendix, *Numerical simulation of trapping by rectification section*.

Numerical results are gathered in Fig. 7a. Starting from a homogeneous spatial distribution of colloids in the channel, the particle population focuses within a band with a stationary and constant width after a short transient of a few oscillations. In these simulations the oscillation period $T_0 = 470$ s is chosen as in the experiments. Except for the first oscillation we check that the wall effects are limited and that the trapped state is not a consequence of the accumulation of the colloids against the wall. Furthermore the colloid density is very well described by a Gaussian distribution (see Fig. 7b) whose center position oscillates with the solute oscillations. These results agree with experimental observations. We also checked that the final trapped state does not depend on the initial condition: a homogeneous as well as a Dirac-like distribution relax to the same steady Gaussian distribution. Additionally the trap state is also independent of the oscillation period $T_0$ varying the period in the same range as in the experiments. Finally, the numerical

**Fig. 6** Sketch of the phenomenon of trapping by rectified oscillations of concentrations. The motion of two particles under DP is shown as arrows: due to log-sensing of DP migration, eqn (1), the velocity profile decreases along the salt gradient (see bottom figures) and the front particles undergo a smaller displacement than the back particles. Over one oscillation, colloids have experienced a net displacement towards the center, and gather in the middle of the cell.

**Fig. 7** Numerical resolution of the particles dynamics under oscillating salt gradients: (a) Spatio-temporal evolution of the colloid density $\rho$, where parameters have been set according to experiments (Fig. 5a): for $D_s = 1360$ μm$^2$ s$^{-1}$, $D_s/D_{DP} = 0.0016$, $D_s/D_{DP} = 0.01$, $f = 800$ μm, $w = 300$ μm and $T_0 = 470$ s. White borders represent the gel walls. The color code ranges from blue (low density) to red (high density). (b) Particle distribution: (blue circles) initial distribution, $t = 0$; (red circles) stationary state distribution; (dashed line) Gaussian profile fit. (c) Evolution of the normalized squared Gaussian width $(\sigma^2/\ell^2)$ as extracted from Fig. 7b) as a function of $D_s/D_{DP}$; (red circles) numerical simulations; (dotted line) fit with linear relationship, according to theoretical prediction (eqn (9)).
simulations permit to test conditions that are not accessible in the experiment to increase the range of accessible $T_0$ such as reducing the gel walls thickness to zero while keeping $\ell$ constant. Modifying $T_0$ once again does not affect the final state. Consequently the final Gaussian state depends neither on the oscillation period nor on the initial distribution of colloids nor on the presence of confining walls.

To conclude on the numerical exploration of the phenomenon, we perform various simulations in which we vary the ratio $D_c/D_{DP}$ in the range $10^{-2}$ to 1. For high diffusiophoretic mobility, the colloid migration is fast and the assumption of time scale separation between the transient gradient and the crossing-time is not valid any more. The colloid population goes from one side to the other crashing systematically on the gel walls. This artificially narrows the colloid distribution. In the low diffusiophoretic mobility regime $D_c/D_{DP} > 1$, the migration of the colloids is too slow compared to the thermal diffusion and no trapped state is obtained. In the range $10^{-2} < D_c/D_{DP} < 1$, the numerical results suggest a width of the Gaussian distribution $\sigma$ scaling as $\sigma \propto \sqrt{D_c/D_{DP}}$, with a prefactor 1/2 (see Fig. 7c).

Asymptotic model. A simple asymptotic interpretation of the above results can be proposed. First, due to the fast salt diffusion, one may neglect the gradient establishment via the diffusion of the boundary conditions. The solute concentration profile is therefore written as:

$$c(x,t) = c_0/2 + c_0(t) x/\ell$$

(7)

where $x$ is the distance to the channel center, $\ell = c/lc$ is the distance over which the gradient establishes and $f(t)$ a time-dependent function, oscillating with the salt concentration oscillation periodicity $T_0$. Typically in our experiments, $f(t)$ is a $\pm 1$ step-function, in the limit of immediate renewal of the side channels solutions, so that $f(t) = 0$ while $f(t)^2 = 1 \neq 0$, with $\langle f(t)^2 \rangle$ the time average over $T_0$.

Now, as in the first part of the study, the mean position $X_0(t)$ of the particle population is expected to obey eqn (4). For small excursions around the center ($X_0 \ll \ell$), one can write

$$dX_0/dt = 2D_{DP}(t)[1-2f(t)(X_0/\ell) + ...]/\ell$$

(8)

In this limit of fast salt oscillations, one expects the distribution in steady state to behave to leading order as $\rho(x,t) = 2\pi x - X_0(t)$, i.e. the distribution is steady in the reference frame of the mean position of the population. Inserting this guess into the Schmoluchowsky equations for the particles gives:

$$J = -D_c \nabla \rho + V_{DP} \rho = -D_c \nabla \rho + \frac{2D_{DP}(t)}{\ell}[1-2f(t)(X_0/\ell)] \times \rho$$

Making the variable change yields $\delta x = x - X_0(t)$ and averaging out the fast salt variables yields to $\langle J \rangle = -D_c \nabla \delta \rho - (4D_{DP}(t)/\ell)^2 \delta x \times \rho$. Altogether, at steady state $\langle J \rangle = 0$, we predict a stationary Gaussian distribution for the particles:

$$\rho(\delta x) \propto e^{-\delta x^2/\sigma^2} \quad \text{with} \quad \sigma = 1/2 \sqrt{D_{DP}/D_c}$$

(9)

The Gaussian distribution is steady in the reference frame moving with the mean position $X_0$ and oscillates as a whole around the channel central position. The asymptotic model stresses the origin of the trapping. The non-linearity of the diffusiophoretic velocity gathers the particles towards the center of the cell, leading to a Gaussian like distribution with a width resulting from the balance between rectified DP migration to the center and the natural Brownian diffusion of the colloids. These results are in full agreement with the experimental observations. Furthermore the expression of the width of the Gaussian distribution is in full agreement with the above numerical resolution of the coupled dynamics (see Fig. 7b, c). Indeed the numerical results collapse on the master curve derived from this asymptotic model with small discrepancies only observed in regimes for which the wall effects are not negligible ($D_c/D_{DP} > 1$) or for which the time-scale separation assumption clearly breaks down ($D_c/D_{DP} < 10^{-2}$).

We also point out that this trapping process can be formally interpreted in terms of an harmonic “osmotic” trapping potential,

$$V_{trap}(x) = \frac{1}{2} k_B T x^2$$

(10)

While the $k_B T$ prefactor suggest an entropic origin, the trapping process is non-equilibrium in its root. Furthermore, the trapping strength is accordingly characterized by an harmonic strength $K = k_B T \sigma^2$. The experimental values for the measured trapping strength $K$ are gathered in Table 2 for various salts. These are compared to the theoretical predictions in which $D_{DP}$ was set to the mobility measured independently in the channel-crossing experiments (Fig. 3). Results in Table 2 show a good agreement between experimental trapping and predicted theoretical values from eqn (9). Note that despite a low diffusiophoretic mobility in LiCl salt, DNA macromolecules are quite effectively trapped by the oscillating concentration gradient. This originates in the strongest non-linearity of the DNA diffusiophoretic migration (see figure Fig. 3b): the front particles nearly stop while the back ones still advance.

A final important remark is that the magnitude of the trapping well is strong: over the cell-chamber scale—with overall size $\ell$—the trapping free-energy well has a depth of $\Delta \mathcal{F} \approx k_B T D_{DP}/D_c \sim 100 k_B T$.

<table>
<thead>
<tr>
<th>Colloid</th>
<th>LiCl</th>
<th>NaCl</th>
<th>KCl</th>
<th>DNA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$</td>
<td>Exp.</td>
<td>22 $\pm$ 2</td>
<td>16 $\pm$ 1.5</td>
<td>N.A.</td>
</tr>
<tr>
<td></td>
<td>Theo.</td>
<td>23 $\pm$ 0.5</td>
<td>16.5 $\pm$ 1</td>
<td>13 $\pm$ 2</td>
</tr>
</tbody>
</table>

*Corresponding to fast gradient oscillations compared to the time evolution of the colloids distribution $T_1 \sim \ell^2/(4D_{DP})$.

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2.4 Pattern symmetry 

We now generalize the previous results to more complex geometries in order to demonstrate the robustness and versatility of the above scenario. To this end we have tested the trapping phenomenon in a circular, “cell shaped” chamber.

Experimental observations. The experimental setup is similar to the previous experiments except for a circular chamber replacing the rectangular one, and modifying the side channels in order to impose a gradient of circular geometry. A sketch of the channels is represented in Fig. 8b and 9b: a circular chamber (650 μm in diameter) is surrounded by two side-channels conveying the salt. The particles—here colloids with 200 nm of diameter—are initially homogeneously spread in the chamber. Two different time-dependent forcings are explored: an antisymmetric forcing where the salt boundary concentrations $c_1$ and $c_2$ are switched periodically between 0 and $c_0$ with antisymmetric phase as in the previous section; and a symmetric forcing where $c_1 = c_2$ switches periodically between 0 and $c_0$ in phase. We want to stress here that the origin of the diffusiophoretic migration depends on the nature of the forcing. The colloids migrate under the imposed concentration gradient in the antisymmetric driving, but the transient gradient—between two steady states of constant salt concentration—is the source of the migration in the symmetric case.

As demonstrated in Fig. 8c and 9c, the salt oscillations again produce a localization of the particles in the cell chamber (see also ESI† movies 3 and 4). Furthermore the symmetry of the pattern depends directly on the symmetry of the driving: one observes a linear localization with a “cat eye” shape for the antisymmetric driving, and a circular egg-shape localization for the symmetric driving. This demonstrates the versatility of the trapping process. Once again, we observe experimentally that the localization process is robust versus the initial distribution of the particles.

Theoretical predictions. These different experimental patterns can be understood on the basis of the theoretical framework discussed above: the colloid dynamics under DP motion are averaged over the fast salt variables and the trapping potential associated with particles localization is then deduced.

We consider the circular cell-like configuration sketched in Fig. 8 and 9. The colloids are embedded in an inner chamber with radius $R$, while the salt boundary condition ring has a radius $r$ (see Fig. 8b). The salt concentration $c(r, \theta, t)$ obeys the diffusion equation

$$ \partial_t c = D_c \Delta c $$

with boundary conditions depending on the nature of the forcing.

Antisymmetric forcing. For the antisymmetric geometry with $T_0$-periodic temporal inversion of the salt concentration in the
lateral channels, the boundary conditions takes the following expression in polar coordinates $r, \theta$:

For $0 < t < T_0/2$, \( c(r = R, \theta, t) = \begin{cases} \ c_0 & \text{if } \theta \in [0; \pi] \\ 0 & \text{if } \theta \in [\pi; 2\pi] \end{cases} \)

For $T_0/2 < t < T_0$, \( c(r = R, \theta, t) = \begin{cases} \ 0 & \text{if } \theta \in [0; \pi] \\ \ c_0 & \text{if } \theta \in [\pi; 2\pi] \end{cases} \)

As for the 1D linear geometry, we neglect transients and consider only the steady concentration profile given by $\Delta c(r, \theta, t) = 0$. The solution of this equation given the boundary conditions takes the form:

\[ c(r, \theta, t) = \frac{c_0}{2} \left(1 + \delta(r, \theta) f(t)\right) \]

with $\delta(r, \theta) = \frac{4}{\pi} \sum_{k', odd} \frac{1}{k} \left(\frac{r}{R}\right)^k \sin[k \theta]$, with $f(t)$ the periodic step-like function with period $T_0$ and $R$ being the radial position at which salt boundary conditions are imposed. As above, the flux of colloidal particles, $J = -D_c \nabla \rho + D_{dp} \nabla \log \rho$, is averaged over the fast salt oscillations, with period $T_0$. The non-linear DP term then simplifies considerably by using $\langle \log \rho \rangle = \log(c_0/2) - \frac{1}{2} \delta(r, \theta)^2$. At this time scale $\langle J \rangle = 0$, so that the colloid density $\rho$ obeys the simple equation

\[ \nabla \left[ \log \rho + \frac{1}{2} \frac{D_{dp}}{D_c} \delta(r, \theta)^2 \right] = 0 \]

The solution to this equation yields the averaged colloid density profile as

\[ \rho[r, \theta] \propto \exp \left[ -\frac{1}{2} \frac{D_{dp}}{D_c} \delta(r, \theta)^2 \right] \]

with $\delta(r, \theta)$ taking the expression above.

**Symmetric forcing.** For the symmetric geometry, a uniform ring of salt oscillates periodically between 0 and $c_0$ and the boundary conditions take the form:

\[ c(r = R, \theta, t) = c_0(\theta, t) = \begin{cases} \ c_0 & \text{for } 0 < t < T_0/2 \\ 0 & \text{for } T_0/2 < t < T_0 \end{cases} \]

This is best rewritten using Fourier series:

\[ c_0(\theta, t) = \frac{c_0}{2} \left(1 + \frac{4}{\pi} \sum_{k', odd} \frac{1}{k} \sin[k \omega t] \right) \]

\[ = \frac{c_0}{2} \left(1 + \frac{4}{\pi} \sum_{k', odd} \frac{1}{k} \text{Im}[\exp(jk \omega t)] \right) \]

with $\omega = 2\pi/T_0$.

Here the steady concentration is uniform and one has to take into account the transient concentration profile. One obtains the salt concentration in the form

\[ c(r, t) = \frac{c_0}{2} \left(1 + \delta(r, t) \right) \]

with $\delta(r, t) = \frac{4}{\pi} \sum_{k', odd} \frac{1}{k} \text{Im}(f_k(r) \exp[jk \omega t])$. For each mode $k, f_k$ is the 2D solution of the diffusion equation and rewrites in terms of the zeroth order Bessel function $I_0(r/\delta_0)$, with $\delta_k = \sqrt{D_k / k \omega}$ the salt diffusive length. By superposition, the salt concentration rewrites explicitly:

\[ c_0(r, t) = \frac{c_0}{2} \left(1 + \frac{4}{\pi} \sum_{k', odd} \frac{1}{k} \text{Im}(\exp(jk \omega t)) I_0(r/\delta_0) I_0(R/\delta_0) \right) \]

Now, taking the log and averaging over the fast salt variables, one gets

\[ \langle \log \rho \rangle = \log(c_0/2) - \frac{1}{2} \frac{D_{dp}}{D_c} \delta_0^2 \]

Finally, keeping only the term for $k = 1$, and expanding for small $r$ and large $R$, as compared to $\delta_0$, one gets the asymptotic colloid density as:

\[ \rho[r] \propto \exp \left[ -\frac{1}{4} \frac{D_{dp}}{D_c} \delta_0^2 r^2 \right] \]

with $\delta_0^{-1} = 8\pi \delta_0^2 \cosh(R/2\delta_0)/R$, with $\delta_0 = \sqrt{D_0 / \omega}$ and $R$ is the radial position at which salt boundary conditions are imposed.

**Discussion**

These predictions for the localization patterns are shown in Fig. 8c’ and 9c’. Altogether they show a good qualitative and semi-quantitative agreement with the experimental results, Fig. 8c and Fig. 9c. The symmetry of the trapping potential depends on the time-symmetry of the salt signal.

**3 Localization by osmotic shock**

In this section, we explore an alternative mechanism, which we call as “osmotic shock”, leading to a strong localization of the colloid population. Once again, this trapping mechanism takes benefit of the logarithmic sensitivity of the diffusiophoretic velocity versus salt concentration: $V_{dp} = D_{dp} \nabla \log \rho$. While in the previous section this log term was harnessed by using rectification of oscillation salt dynamics, here we rather make use of the extreme sensitivity of DP transport in vanishing electrolytes concentration. Indeed, from the above expression, it is expected that a vanishing gradient can lead to measurable velocity provided that the solute concentration is low enough, so that $\nabla \log \rho$ is finite. We explore further this point via experiments in this “osmotic shock” configuration.

**3.1 Experimental observations**

We start with a solution of 200 nm latex colloids in a LiCl salt solution (concentration $c_0 = 100$ mM) with buffer (Trizma 1 mM, pH 9). The colloidal suspension is enclosed in
condition chamber relaxes by diffusion and finally reaches the equilibrium concentration $c$. Initially, the colloid solution and the gel are in a LiCl salt solution of typically 100 mM of salt. For $t < 0$, salt concentration is thus homogeneous, with value $c_0$ in the system. (a) Initial colloids distribution (fluorescence image). A $t = 0$, boundary conditions $c = 0$ is imposed by a syringe pump. For $t > 0$, the concentration profile relaxes to reach the long time limit $c = 0$. (b) The system undergoes an “osmotic shock” and the colloids move towards the high concentration of salt, e.g., the center of the chamber. The migration lasts up to 10 min leading to an efficient focusing of the colloid population. The colloid distribution thereafter spreads by Brownian diffusion.

A microfluidic chamber filled with the same LiCl salt solution (see Fig. 10a). At $t = 0$, a solution containing only buffer is injected with the syringe-pump and the boundary conditions for the salt abruptly go from $c = c_0$ to $c = 0$. The salt concentration in the chamber relaxes by diffusion and finally reaches the equilibrium condition $c = 0$ imposed by the boundary conditions. In relation with the presence of a salt gradient the colloids strongly concentrate by diffusiophoresis in the center of the cell, see Fig. 10b and movie 5 (ESI†). Interestingly the migration is observed to occur up to long times, typically $\sim$ 10 min, while in this geometry the salt concentration is expected to reach a spatially homogeneous state after a much smaller time $\sim$ 1–2 min. For longer times, the Brownian diffusion dominates and the distribution of colloids is again slowly widened by the Brownian motion of the colloids.

### 3.2 Principle and theoretical description

Of course the directed motion of the colloids to the center of the cell takes its origin in the DP migration as the salt concentration in the center of the chamber. The migration lasts up to 10 min leading to an efficient focusing of the colloid population. The colloid distribution thereafter spreads by Brownian diffusion.

Fig. 10 Localization by osmotic shock. Circular well is 650 μm in diameter with gel walls 125 μm wide $t = 900$ μm; scale bar 200 μm. Initially, the colloid solution and the gel are in a LiCl salt solution of concentration $c_0 = 100$ mM of salt. For $t < 0$, salt concentration is thus homogeneous, with value $c_0$ in the system. (a) Initial colloids distribution (fluorescence image). A $t = 0$, boundary conditions $c = 0$ is imposed by a syringe pump. For $t > 0$, the concentration profile relaxes to reach the long time limit $c = 0$. (b) The system undergoes an “osmotic shock” and the colloids move towards the high concentration of salt, e.g., the center of the chamber. The migration lasts up to 10 min leading to an efficient focusing of the colloid population. The colloid distribution thereafter spreads by Brownian diffusion.

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The long timescale for the migration of the colloids is consequently surprising and puzzling at first.

As mentioned above, a key point of diffusiophoresis with electrolytes is that due to the expression of the diffusiophoretic velocity $V \propto \nabla c$ the diffusiophoretic drift is very sensitive to regions where the concentration vanishes ($c \rightarrow 0$), as long as $\frac{\nabla c}{c}$ is finite. As we now show, this log-sensing of the velocity is at the origin of the long term evolution—of order of 10 mins—of the colloid migration. We now turn to the time dynamics of the colloidal density $\rho(r, t)$ in this osmotic shock configuration. The description assumes a 2D circular geometry and the parameters will be set to the experimental values.

**Solute dynamics in an osmotic shock configuration.** The salt concentration $c$ obeys the diffusion equation, together with the boundary conditions at the chamber perimeter. For the osmotic shock the boundary conditions are $c(r = R, t < 0) = c_0$ and $c(r = R, t > 0) = 0$ (same notations as in the previous section).

Looking for separable solutions, $c = f(t)g(r)$, we obtain the solution for the time-dependent diffusion equation in terms of zeroth order Bessel function of first kind $J_0$:

$$c(r, t) = \sum_n a_n e^{-K_n t} J_0 \left( \frac{r}{D_s} \right)$$

(16)

with $K_n$ defined as $K_n = \alpha_n^2 D / R^2$, with $\alpha_n$ the $n^{th}$ zero of $J_0$ and $D_s$ the salt diffusion coefficient.
The coefficients \( a_n \) are defined by the initial condition \( c(r, t = 0) \):

\[
c_0 = \sum_n a_n J_0 \left( r \sqrt{\frac{K_c}{D_c}} \right), \quad \text{for} \quad r < R
\]  

(17)

In the long-time limit, as \( K_c > 0 \) and increases with \( n \), only the first term in eqn (16) remains and

\[
c(r, t) = a_i e^{-D_i t} J_0 \left( a_i \frac{r}{R} \right)
\]  

(18)

with \( a_1 = 2.4 \) the first zero of \( J_0 \). It follows that the diffusiophoretic velocity takes the form:

\[
V_{DP} = D_{DP} \nabla c / c = D_{DP} \nabla \log J_0 \left[ a_1 \frac{r}{R} \right]
\]  

(19)

A key result is therefore that the (radial) asymptotic velocity of the colloids is time independent! This result is confirmed by a full resolution of the salt concentration profile, as shown in Fig. 11b. This underlines the role of the log-sensing of the diffusiophoretic transport in the long time evolution of the colloid distribution during the osmotic shock. The DP migration is accordingly expected to last indefinitely!

**Fokker–Planck equation for the colloid evolution.** Some further predictions may be obtained from the equation for the colloid time-dependent evolution. As a first approximation, we use the above form for the diffusiophoretic drift. This is strictly valid for sufficiently long times \( t > K_t^{-1} \sim 30 \text{s} \), but in the present problem there is a time-scale separation between the solute dynamics and the colloid dynamics (evolution over \( \sim 10 \text{ min} \)), so that this is a reliable approximation.

One may then write the equation for the colloid density \( \rho \) as

\[
\partial_t \rho = \nabla \cdot \left[ -D_{DP} \nabla \log J_0 \left[ a_1 \frac{r}{R} \right] \times \rho \right] + D_c \nabla^2 \rho
\]  

(20)

The stationary solution of this equation with vanishing flux is given by:

\[
\rho(r) \propto \left( J_0 \left[ a_1 \frac{r}{R} \right] \right)^\beta
\]  

(21)

with \( \beta = D_{DP}/D_c \sim 145 \).

Coming back to the time dependent equation for the colloids, an expansion can be performed for small distances \( r \) from the center. Accordingly, an approximated form for the diffusiophoretic drift term of eqn (20) can be obtained using

\[
\nabla \log J_0 \left[ a_1 \frac{r}{R} \right] = -\frac{1}{2} \frac{a_1^2}{R^2} \times r
\]  

(22)

This leads to a Fokker–Planck equation for \( \rho \):

\[
\partial_t \rho = \nabla \cdot \left[ \frac{D_{DP}}{2} \frac{a_1^2}{R^2} \times \rho \right] + D_c \nabla^2 \rho
\]  

(23)

This can be rewritten as

\[
\partial_t \rho = \frac{1}{\tau} \nabla \cdot [\tau \rho + \sigma^2 \nabla \rho]
\]  

(24)

with \( \tau^{-1} = \frac{1}{2} D_{DP} \frac{a_1^2}{R^2} \) and \( \sigma^2 = \frac{2}{a_1^2} \frac{D_c}{D_{DP}} \times R^2 \). Note that \( \tau = \sigma^2 / D_c \). This is the so-called Orstein–Uhlenbeck process.\(^*\) The stationary solution is a Gaussian with width \( \sigma^2 \):

\[
\rho(r, t) \propto \exp \left( -\frac{r^2}{2\sigma^2} \right)
\]  

(25)

which is in full agreement with eqn (21), as \( J_0 \) can be approximated by a Gaussian with very good accuracy.

The solution of this Orstein–Uhlenbeck equation can be expressed analytically.\(^*\) A more detailed derivations can be found in the appendix. In the present 2D geometry, it finally gives for the colloid density:

\[
\rho(r, t) = \rho_0 A(t) e^{-\alpha t} \int_0^R 2\pi r' dr' J_0(2\alpha \beta r') e^{-\alpha \beta r'^2} \]  

(26)

with \( J_0 \) the zero order Bessel function and \( A(t) = [2\pi \sigma^2(1 - e^{-2\gamma t})]^{-1} \), \( \gamma = \tau^{-1} \), \( \alpha(t) = [2\sigma^2(1 - e^{-2\gamma t})]^{-1} \) and \( \beta(t) = e^{-\gamma t} \).

**Comparison with the experiments.** To compare with the experimental results, we focus on the time dynamics of the width \( \Gamma(t) \) of the colloid distribution. Here we define \( \Gamma(t) \) as \( \rho(t) = \Gamma(t) \) at \( t = 0, \rho(t) = e \times 2.71 \ldots \). The experimental result is shown in Fig. 12. On the theoretical side, this parameter is computed numerically from the prediction in eqn (26).

We first plot as a green dashed line in Fig. 12 the theoretical prediction using as input parameters the experimental values for \( D_c = 2 \text{ \mu m}^2 \text{ s}^{-1} \) and \( D_{DP} = 290 \text{ \mu m}^2 \text{ s}^{-1} \) (measured independently in DP migration experiments, see section 1.2), together with the geometrical characteristic sizes \( R = 450 \text{ \mu m} \) and \( R = 325 \text{ \mu m} \). Using

\[
\text{Fig. 12 Radius of the colloid distribution versus time. Comparison to theoretical predictions. Radius } \Gamma(t) \text{ measured in experiments from the colloid density profiles (blue symbols). The green dashed curve is the prediction using the experimental parameters } D_c = 2 \text{ \mu m}^2 \text{ s}^{-1} \text{ and } D_{DP} = 290 \text{ \mu m}^2 \text{ s}^{-1} \text{ (measured independently by diffusiophoretic migration experiments), } R = 450 \text{ \mu m} \text{ and } R = 325 \text{ \mu m} \text{ yielding } \sigma = 22.3 \text{ \mu m} \text{ and } \tau = 250 \text{ s} \text{. The red dashed curve is obtained with the same value of } \sigma = 22.3 \text{ \mu m} \text{ and } \tau = 290 \text{ s, chosen to obtain a 'best fit' to the experimental data. The dashed black line is the purely diffusive motion: } \Gamma(t) = \sqrt{R_{ref}^2 + 4D_c(t-t_{ref})} \text{ with the values } R_{ref} = 94 \text{ \mu m} \text{, } t_{ref} = 1115 \text{ s, taken as references.}
the above expressions, one obtains $\sigma = 22.3 \mu m$ and an exponential decay over a time $\tau = \sigma^2/D_c \sim 250 s$. This prediction is in qualitative and semi-quantitative agreement with the experiments. A much better agreement can be obtained by relaxing the constraint on the relaxation time and using $\tau = 290 s$ as a “best fit” while keeping the value of $\sigma$ to the predicted one: see red dashed line in Fig. 12. As seen on this figure, a very good agreement is obtained between the theoretical predictions and the experimental results, at least up to time of 500 s. This shows that this scenario does capture the physics at work in this first regime. However, for longer times ($t > 500 s$), the system does enter a new dynamical regime with the radius expanding again.

As we now show, this second regime occurs due to the presence of a small but finite buffer concentration in the solution. Indeed, without buffer, one would expect a time-independent DP velocity towards the center of the cell and a decreasing function $\Gamma(t)$. The slight increase of the radius $\Gamma$ of the distribution at long time, for $t > 500 s \approx 2\tau$, suggests that the DP mechanism becomes inefficient at long times.

The finite buffer concentration does actually act as a cut-off for the driving force of the DP migration during the osmotic-shock process. Indeed, while fixing the pH (to $pH = 9$), the buffer adds some charged chemical species in the solution, the concentration of which—though minute—does compare with the bare salt concentration in the solution. Indeed, Tris (Trizma, 1 mM, $pH 9$, Sigma Aldrich), is a neutral species which equilibrates with its charged acidic counterpart Tris$^+$ ($pK_a = 8.06$), with concentration $[\text{Tris}^+] \approx 3.10^{-8} M$. The presence of other chemical species is negligible in the present context.

Now, the presence of such supplementary chemical species is expected to modify the so-called electrophoretic contribution to the diffusiophoretic migration.$^4$ As discussed by Prieve and co-workers (see ref. 1 for a review), this contribution stems from the electrophoresis of the colloidal particles under the electric field generated because the diffusion coefficients of various ions are not equal. For a symmetric electrolyte, this electric field writes $E_x = k_B T/\varepsilon \beta \nabla V_{logc}$, with $\beta = (D_+ + D_-)/(D_+ + D_-)$ the asymmetry in salt diffusion coefficients. This expression for $E_x$ is deduced from the condition of a vanishing local electric current far from the colloids.$^4$ Now with the supplementary charged specie Tris$^+$, with concentration $c_T$, one may show that the condition of a vanishing current modifies the expression for the electric field to $E_x = k_B T/\varepsilon \beta \times \nabla c(c + c_{c,o})$, with $c_{c,o}$ an effective cut-off concentration defined as $c_{c,o} = D_T/(D_+ + D_-) \times c_T$, with $D_T$ the diffusion coefficient of the Tris$^+$. Typically, one expects $D_T/(D_+ + D_-) \approx 0.15$. Altogether the electrophoretic contribution to the driving force of DP migration can be rewritten as

$$V_{DP}^c = \frac{\nabla c}{c + c_{c,o}}$$

where $c_{c,o} = \alpha c_b$ with a numerical prefactor $\alpha = 4.10^{-3}$ and $c_b$ the Tris buffer concentration. Finally, putting numbers shows that this electrophoretic contribution is the dominant contribution to diffusiophoresis for LiCl as a salt$^4$ and we assume $V_{DP} = V_{DP}^c$.

The cut-off concentration is extremely small, as $c_{c,o} = 4.10^{-5} M$, but the sensitivity of DP migration to small concentrations is able to detect it. For long times, such that $\Gamma(t, t) < c_{c,o}$, $\nabla c(c + c_{c,o}) \approx \nabla c/c_{c,o} \approx 0$ and so does the diffusiophoretic velocity. Typically, this occurs for a time $T_{cut-off} \sim \frac{R^2}{D_c} \times \log(c_b/c_{c,o})$ (see eqn (18)).

For experiments in microfluidic cells, $R = 450 \mu m$ with LiCl salt, $D_c \sim 1350 \mu m^2 s^{-1}$, one gets a cut-off time $\sim 5-6$ min, in fair agreement with the experiments. This effect is evidenced in the inset of Fig. 11b, where $\partial_t V_{DP}(t = 0, t)$ is plotted versus time: this quantity accounts for the “restoring force” leading to the trapping of the colloids in the center. This force is seen to decay to zero in the presence of a buffer, while reaching a constant stationary value in the absence of the buffer. Note that in this plot the salt concentration is obtained by a numerical resolution of the full diffusion equation for the salt density profile.

Finally, in the long time limit, $t > T_{cut-off}$ (with $T_{cut-off}$ the cut-off time introduced above), the trapping becomes ineffective and the size of the colloid distribution will thus increase again due to Brownian diffusion, according to $R^2 \sim D_c t$. We have plotted this prediction on Fig. 12 (black dashed line), $R(t) = \sqrt{R_{cut-off}^2 + 4D_c(t-t_{ref})}$, with $R_{ref}$ the value of the radius taken at a reference time $t_{ref}$. This is in very good agreement with the tendency observed experimentally.

### 3.3 To sum up on localization by osmotic shock

Altogether the temporal dynamics of the localization induced by osmotic shock is a two step process. The radius $R(t)$ first follows an exponential decay for $t < T_{cut-off}$ associated with the sensitivity to vanishing concentrations of electrolyte solution of diffusiophoresis. Then, $R(t)$ enters a diffusive regime for $t > T_{cut-off}$. The buffer acts as a cut-off for the diffusiophoretic migration and the thermal motion of the particles dominates the dynamics in this regime. The cut-off time $T_{cut-off} = \tau \times D_{DP} D_c \times \log(c_b/c_{c,o}) \sim \tau$ accounts for the cut-off role of the buffer on the osmotic shock.

As a final remark, we note that, had we used a charged buffer instead of the present neutral Tris molecule (Trizma), the cut-off concentration would have been much higher (with $c_{c,o} = c_b$), and this would have accordingly stopped the DP migration much earlier during the osmotic shock.

### 4 Conclusions

In this paper, we have measured and characterized the diffusiophoretic migration of various colloids particles—latex colloids or biological macromolecules as DNA—in a spatially and temporally controlled gradient thanks to especially devised hydrogel microfluidic techniques. We report a logarithmic dependence of the diffusiophoretic velocity of the colloids in gradients of electrolytes in agreement with theoretical expectations for these systems.

Further experimental evidences of trapping of colloids are unveiled based on the specific functional dependence of the diffusiophoretic velocity on the gradient of the logarithm of the salt concentration. The non-linearity of this expression is harnessed to induce localization of particles by rectification of concentration oscillations. Furthermore the extreme sensitivity of the logarithmic-sensing to vanishing salt concentrations was exploited to strongly trap particles by an “osmotic shock”. These
two trapping mechanisms are discussed and rationalized theoretically. They also prove to be versatile and robust in regards to the experimental conditions.

Our results raise a number of questions which should be tackled in the future. First, one lacks of description for the diffusiophoresis of polymer and polyelectrolytes under solute and salt gradients. As we have seen in the present paper, some discrepancies with predictions obtained assuming colloidal spherical particles are observed. A novel theoretical framework should be proposed. Second, the log sensitivity which we extensively discussed raises the question of the limit of sensitivity of diffusiophoretic migration for vanishingly small salt concentration, close to ultra-pure water conditions. Indeed the log-sensing suggest that DP migration remains effective down to very small salt concentrations, provided that \( \nabla c \) remains finite. This is a counter-intuitive result, which should be explored more specifically. In particular in a ultra-dilute regime for the salt in which distances between ions becomes larger than the particle size, the classical hydrodynamic description of DP is expected to fail and should be replaced by a novel approach which remains to be elaborated.

As a final word, one may raise the question of the pertinence of the generic mechanisms discussed here for biological systems, beyond diffusiophoretic migration itself. Indeed concentration gradients of chemicals are at the core of many biological processes and a cornerstone in the field of spatial cell biology e.g. the building up of the spatial self-organization both at the supra\(^9\) and intra\(^3\)\(^2\) cellular levels. In a different context, pollen tube growth was shown to correlate to ion (\( H^+ \) and \( Ca^+ \)) oscillations.\(^9\) While the origin of migration in these systems is not related to diffusiophoresis, chemotaxis of biological materials usually involves non-linear sensing, which is the main requisite for rectification effects to occur. Though purely speculative, the role of such effects would deserve a specific exploration.

Appendix: Materials, preparation and methods

Soft lithography of microfluidic masks

The design of the channel is obtained through classical soft lithography techniques. Briefly, the desired features are designed on Adobe Illustrator and printed at 3600 dpi on transparent films and therefore reproduced on a SU8 permanent epoxy negative photoresist (SU8-2100, Microchem). Experimental parameters are fit accordingly to obtain channels with thickness ~120 \( \mu \)m. After development, the mold is finally hard-baked during 1 h to improve the mechanical resistance to thermal constraints on the mold.

Hydrogel microfluidic channels

**Hydrogel preparation.** Agarose hydrogel powder (Agarose ME, for biochemistry, Acros) is weighed with a precision balance and added to ultra-pure water (resistivity 18.2 M\( \Omega \), MilliQ) up to a 5% w/v solution.\(^*\) The solution is vortexed and then microwaved at 1500 W until boiling. It turns out to be transparent and homogeneous hydrogel solution. The liquid hydrogel is poured in a covered beaker on a hotplate at 80 \( ^\circ \)C and gently stirred at typically 100–200 rpm.

**Agarose gel microchannels.** The SU8 master is placed on a hotplate at 75 \( ^\circ \)C and the design of the channels is covered by ~1.5 ml of the hot liquid agarose solution. The silicon wafer is then removed from the hotplate and a plexiglas manifold with a PDMS spacer is pressed onto the mask during 40 s. The PDMS spacer is a rectangular ring with a thickness ~700 \( \mu \)m higher than the depth of the channels (~120 \( \mu \)m) and consequently defines the shape and the thickness of the gel stamp. The device is allowed to cool down at room temperature during one minute for settling of the hydrogel matrix. The agarose stamp is therefore carefully peeled off the mask and stored in ultra-pure water at 6 \( ^\circ \)C until subsequent use. The inlets and outlets of the channels are holed with a metal tip just prior use of the agarose channels.

**Preparation of a microfluidic device.** The classical sealing of PDMS microchannels is based on the covalent bonding of the PDMS on plasma activated silica. This is not possible with agarose microchannels. We hence manufactured a mechanical system to impose homogeneous pressing on the channels and thus proper sealing of the device. A clean coverslip (Roth, thickness 130–170 \( \mu \)m) is placed on an aluminium framework machined for convenient microscope observation. Particles under investigation are introduced in the central microfluidic chambers prior to the beginning with a drop deposit of the colloidal solution on the glass slide. An agarose stamp with drilled inlets and outlets is placed in the PDMS spacer frame used for molding and then sandwiched between a glass coverslip and a plexiglas manifold with channels facing the coverslip. A plexiglas press allows to apply homogeneous and sufficient pressure to ensure proper sealing of the microfluidic device.

**Running an experiment**

The hydrogel microfluidic is then ready for use and only needs to be completed with inlets and outlets to carry experiments. The side-channels, used to impose the solute, here salt, concentration boundary condition in the system, are filled with a double syringe pump (Kd Scientific) with flow rate \( Q = 0.1 \) ml min \(^{-1}\) by means of 5 ml plastic syringes (Braun). The syringes are filled with buffer (Trizma, 1 mM, pH 9, Sigma Aldrich) or with a 100 mM solution of salt (typically LiCl or NaCl) in Tris-buffer. Salt molecules diffuse freely in the patterned agarose gel while the solid hydrogel matrix prevents from convective flow between channels. Overall, side channels thus allow to set a concentration boundary condition, and the transverse gradient of salt in the central channel is linear and solution of the steady diffusion equation \( \Delta c = 0 \) (see Fig. 1b). Temporal control is achieved with a manual microfluidic switch (V140D, Upchurch) to reverse the role of the concentration boundary conditions. Finally, we use two types of motile particles: polystyren-carboxylated fluorescent colloids (F8888 200 nm, Molecular Probes, 2% w/v), diluted 10 times in Tris buffer (1 mM Trizma, pH9), and fluorescent phage-\( \lambda \) DNA (48 kbp, Fermentas, Germany) at a concentration of 0.9 nM in Tris-EDTA buffer (1 mM Tris, 0.1 mM EDTA, pH 7.6).

\(^*\) This concentration gives a good compromise for both a good mechanical response in the solid phase and a sufficiently slow aging and settling of the liquid phase.
All the observations are carried out with an inverted microscope (DMI4000B, Leica®) and a fluorescence camera (Orca, Hamamatsu®). The fluorescence signal is recorded with a 20× objective (ELWD, corrected for glass 0–2 mm, N.A. = 0.4, 11506204, Leica) at 0.1 Hz.

Experimental validation of the setup

In this section, we underline a few experimental tests and cares validating the use of the hydrogel microfluidic device.

Experimental checks. We first check that without any salt gradient the colloids dynamics is purely Brownian. A slight longitudinal drift can be observed in some experiments by the following of a few bunches of colloids as markers. The upper bound for this occasional drift speed is 50 nm s⁻¹ small compared to the diffusiophoretic velocity of the particles (VDP ≈ 1 μm s⁻¹) and thus negligible. We infer this a Darcy flow through the porous gel. The pressure gradient originates in the pressure drop due to the Poiseuille flow in the side channels. The pressure gradient induced by the flow in lateral channel is of order \( \nabla P \approx \frac{h}{h + 1} U \) with \( h \) the viscosity of the solution, \( h \approx 100 \mu\text{m} \) the height of the microfluidic chamber and \( U \) the velocity of the injected solution. This pressure gradient is transmitted through the gel walls to the microfluidic chamber and induces flow along the chamber thanks to the porosity of the gel. At steady state, the drift in the chamber is related to the pressure gradient by the Darcy relationship \( V_d = -\frac{2}{\eta} \nabla P \) (b). For a flow velocity \( U \approx 5 \text{ cm s}^{-1} \) and a Darcy permeability \( \kappa \approx 500 \mu\text{m}^2 \) (extracted from the literature for a 3% agarose gel²⁴), we obtain \( V_d \approx 2.5 \text{ nm s}^{-1} \) which is in reasonable agreement with what we observed experimentally. This observation may appear trivial but actually constitutes an essential test. First, the reproducible and reliable absence of leakage is not an easy task to reach in microfluidics. Second, devising an observation chamber maintained at rest with residual drifts of only a few nm s⁻¹ goes far beyond the standard accuracy required in microfluidics even for pressure-driven flows.

Sedimentation. We use 200 nm latex colloids with a sedimentation length \( \delta = k_B T m g \approx 100 \mu\text{m} \), with \( k_B \) the Boltzmann constant. \( T \) the room temperature, \( m \) the boyant mass of colloid and \( g \) the gravity. \( \delta \) is thus of the same order of magnitude as the height of the microfluidic chamber (\( h \approx 120 \mu\text{m} \)) which provides a reasonable vertical uniformity of the colloid concentration. Additionally, the sedimentation velocity is given by \( v_{sed} = mg/6\pi\eta R \), \( \eta \) being the viscosity of the fluid and \( R \) the radius of the colloid. For these particles \( v_{sed} \approx 1 \text{ nm s}^{-1} \) which ensures a weak effect of the sedimentation during the typical time of an experiment (~1–2 h).

Determination of \( X_0(t) \) from fluorescence measurements

The position of the maximum \( X_0(t) \) of the colloid population is defined from the fluorescence images with Matlab as follows. First, the intensity profile is averaged on the all picture to give a 1D profile. Then the maximum of the profile is determined. In order to limit the influence of intensity fluctuations in the profile, a local quadratic fit of the intensity is carried to determine the position of the maximum of intensity, \( X_0 \).

Appendix: Numerical simulation of trapping by rectification

In a first step, the coupled eqn (6) are solved numerically using Matlab®. The geometry as well as the boundary conditions match the experiments. The salt concentrations in the side channels oscillate with a stepwise function of period \( T_0 \). Accordingly the gel walls are implemented in the numerical simulations as impermeable frontiers only for particles and a free-diffusion medium for salt.

The problem is made dimensionless, using \( \ell \) as the unit of length and determining the unit of time with \( D_s \). Additional variables are the following: \( \tilde{z} = \ell z/\ell, \tilde{t} = \ell^2 t/\ell D_s \) and the diffusion coefficient expresses in units of the salt diffusivity: \( D_s = D/D_s \) where \( D_s \) and \( D_s \) are the diffusivities of the constituent ions and \( z_+ \) and \( z_- \) valence.¹ In the following, \( D_s \) is set to 0.0016 to match the experimental value for colloids of diameter \( \Phi = 200 \text{ nm} \) in a LiCl salt. Finally, the coupled partial equations are solved with Matlab in 1D with \( D_s/D_s \) as the variable parameter. Results are presented in Fig. 7.

Appendix: Resolution of the Orstein–Uhlenbeck process for the colloid density

The dynamics of the colloid density in the osmotic shock is given by the Orstein–Uhlenbeck equation eqn (24). It is solved as follows. First the propagator—solution of eqn (24) with a point-like initial condition, \( P(0, t = 0|r') = \delta (r - r') \)—takes the form in a \( d \) dimension space:

\[
P(r, t|r') = \frac{1}{(2\pi \sigma^2 (1 - \exp(-2\gamma t)))^{d/2}} \times \exp \left[ \frac{1}{2\sigma^2} \frac{(r - e^{-\gamma t}r')}{(1 - e^{-2\gamma t})} \right]
\]

(28)

with \( \gamma = \tau^{-1} \). Then the complete solution for the colloid density is given by “propagating” the initial colloid distribution:

\[
\rho(r, t) = \int d' \rho_0(r') \times P(r, t|r')
\]

(29)

with \( \rho_0(r) \) the initial condition for the colloid density. In line with the experimental conditions, we assume a uniform initial density over a circle of radius \( R \) (not to be confused with \( R \) the radius of the salt boundary condition), so that

\[
\rho(r, t) = \rho_0 \int_{|r'| < R} d' P(r, t|r')
\]

(30)

This integral can be calculated after some straightforward—but cumbersome—calculations. In the present 2D geometry, this gives with \( J_0 \) the zero order Bessel function:

\[
\rho(r, t) = \rho_0 A(t) e^{-\alpha z^2} \sum_{\alpha = 0}^\infty 2\pi \alpha \rho(r'J_0(2\alpha \beta r')e^{-\alpha^2 r'^2/2})
\]

(31)
where we introduced: $A(t) = [2\pi \sigma^2(1 - e^{-2\gamma t})]^{-1}$ with $\gamma = \tau^{-1}$ and $\alpha(t) = [2\sigma^2(1 - e^{-2\gamma t})]^{-1}$, $\beta(t) = e^{-\gamma t}$.

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