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# Nanoparticle Taylor dispersion near charged surfaces with an open boundary

Alexandre Vilquin,<sup>1,2,\*</sup> Vincent Bertin,<sup>1,3,4,\*</sup> Elie Raphaël,<sup>1</sup>  
David S. Dean,<sup>3,5</sup> Thomas Salez,<sup>3,†</sup> and Joshua D. McGraw<sup>1,2,‡</sup>

<sup>1</sup>*Gulliver UMR 7083 CNRS, PSL Research University,  
ESPCI Paris, 10 rue Vauquelin, 75005 Paris, France*

<sup>2</sup>*IPGG, 6 rue Jean-Calvin, 75005 Paris, France*

<sup>3</sup>*Univ. Bordeaux, CNRS, LOMA, UMR 5798, F-33405, Talence, France*

<sup>4</sup>*Physics of Fluids Group, Faculty of Science and Technology,  
and Mesa+ Institute, University of Twente, 7500AE Enschede, The Netherlands.*

<sup>5</sup>*Team MONC, INRIA Bordeaux Sud Ouest, CNRS UMR 5251,  
Bordeaux INP, Univ. Bordeaux, F-33400, Talence, France.*

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The dispersion of microscopic particles in shear flows is influenced both by advection and thermal motion. At the nanoscale, the interactions between such particles and their confining boundaries, along with their size, cannot be neglected. Here, using evanescent-wave microscopy with sub-micrometric observation zones, we study the transport of charged nanoparticles in linear shear flows, near a charged, planar wall on one side, and an open, particle-consuming boundary on the other side where the particle leaves the observation zone. By varying the concentration of electrolytes, we show how electrostatic interactions between particles and surface affect dispersion. In addition, an absorption-like condition at the open boundary induces an exponential decay of the particle number, which alters the transport efficiency. The combination of these two effects reduces the overall dispersion by an order of magnitude, as captured by our theoretical model. Our findings might have implications in biological contexts as well as in technological devices based on the transport of confined diffusive objects at small scales.

A key aspect of microscale material transport is the coupling between advection by a flow and Brownian diffusion across the flow's streamlines. The diversity of sampled velocities over a given time frame dominates the extent to which material is spread out, and dispersion enhancement can be orders of magnitude compared to pure molecular diffusion. This *Taylor-Aris dispersion* [1] is the principal mechanism for solute dispersal in several natural and technological contexts: examples include nutrient and drug transport [2, 3], chemical reactions in porous media [4, 5] or in a variety of biological processes [6–11]. At nanometric distances from bounding surfaces, particles cannot be considered as simple tracers since they are subject to: physico-chemical forces of intermolecular origin (*e.g.* electrostatic or van der Waals [12]); hydrodynamic interactions with the boundary [13–16] which reduce the mobility close to the surface; as well as reaction/absorption at the interface [4, 17–22]. Crucially, such interactions may modify the diffusion-mediated velocity sampling and therefore the extent of dispersion.

Taylor dispersion has many applications in situations where such nanoscale physico-chemical interactions are important, with biophysical ones as emblematic examples. As such, the seminal theoretical work of Taylor has been extended [23] to cases of non-spherical [24] or active [25, 26] colloids, dispersion near pulsating walls [27] and in particular, with interacting and absorbing inter-

faces [4, 18–21, 28–31]. Despite this extensive theoretical effort, only a few experiments focussed on the strong effect of these interactions or the absorption [32–34]. Particle absorption or chemical reactions at the interfaces modify dispersion in a non-trivial way [22, 27, 31]. If the absorption is weak, the relative spreading is enhanced since the concentration is reduced near the surfaces. At larger absorption rates, the concentration decrease is too fast for an efficient redistribution to occur, which reduces Taylor dispersion. The latter case is also accompanied with a substantial reduction of the total number of transported particles. Such a reactivity is critical for *e.g.* drug delivery [35, 36] or monitoring chemical reactions [37–39], determination of molecular diffusion coefficients [40–42], protein conformation [43], or peptide speciation [44], to give but a few examples.

Here, we study the dispersion of nanoparticle ensembles in a linear, near-surface flow by using evanescent-wave microscopy. Elaborating further on a previous dynamical study [45], this experimental setup allows for a precise study of Taylor dispersion at the nanoscale. Particularly, we systematically vary the weight of surface interactions in the dispersion process by: (*i*) tuning the repulsive electrostatic interaction between the nanoparticles and one surface; and (*ii*) exploiting the constitutive finite observation zone and open boundary. Specifically, as schematically indicated in Fig. 1(a), particles inevitably leaving the observation zone are treated as permanently absorbed. Using an extended version of the moment theory [46–50], we show that an order-of-magnitude reduction of the dispersion occurs when both types of interactions, *i.e.* (*i*) and (*ii*), are present, as

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\* The authors contributed equally

† thomas.salez@cnrs.fr

‡ joshua.mcgraw@cnrs.fr

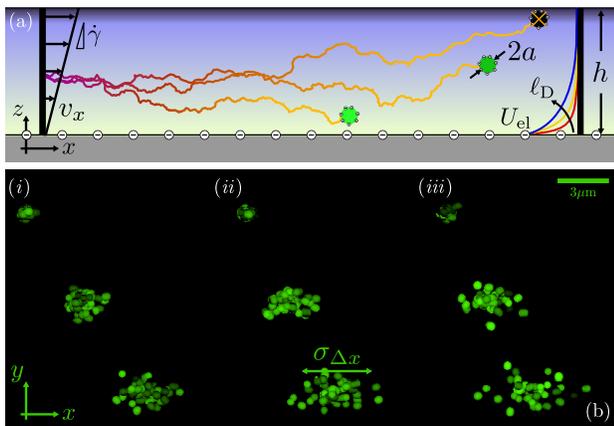


Figure 1. (a) Side-view schematic of the experimental setup addressing Taylor dispersion at the nanoscale. In a channel of height  $h$ , nanoparticles with radius  $a = 55$  nm are advected by a linear shear flow,  $v_x(z) = \dot{\gamma}z$ , and diffuse. An electrostatic potential  $U_{el}(z)$  characterises the repulsion between the particles and the bottom surface at  $z = 0$ , with various Debye lengths  $\ell_D$ . Particles that reach the upper surface at  $z = h$  are below the sensitivity threshold of the camera, and are thus considered as absorbed. (b) Superposition of experimental trajectories ( $x$ - $y$  top-view) with lag times  $\tau = 2.5$  ms (top row), 25 ms (middle row), and 50 ms (bottom row), showing three successive positions of fluorescent nanoparticles in (i) pure water, (ii) 5.4 mg/L NaCl aqueous solution, and (iii) 54 mg/L NaCl aqueous solution.

compared to the case in which such interactions are absent.

We used objective-based, total internal reflection fluorescence microscopy (TIRFM) [51] to study the nanoscale motions of colloidal particles (Fisher Scientific F8803), with radius  $a = 55$  nm, advected by a pressure-driven flow (Elveflow OB1, pressure drops from 20 to 70 mbar) as schematically indicated in Fig. 1(a). Particles were observed at 400 Hz (Andor Neo-SCMOS) in a  $20 \mu\text{m}$ -tall polydimethylsiloxane (Dow RTV) microchannel with  $200 \mu\text{m}$  width and 8 cm length. The fluorescence was achieved using an excitation laser (Coherent Sapphire, wavelength 488 nm) with the fluorescence intensity,  $I$ , related to the apparent particle altitude,  $z_{app}$ , through  $z_{app} - a = \Pi \ln(I_0/I)$ . Here  $\Pi$  is the evanescent decay length and  $I_0$  is the intensity of a particle with center at  $z = a$ . We varied the laser power  $P_{laser}$  from 15 to 150 mW, allowing for a variation of the height  $h$  of the observation zone. The particles' electrostatic interaction with the solid glass surface was tuned by changing the concentration of NaCl (Sigma) in ultrapure water (18.2 M $\Omega$  cm, MilliQ). A particle-tracking algorithm (see videos in the Supplementary Information, SI) allowed us to study approximately  $10^5$  particle trajectories for this study; ensembles of *ca.*  $10^2$  such trajectories with three delay times per column are shown in Fig. 1(b). From these ensemble trajectories, the linear near-wall velocity profile  $v_x(z) = \dot{\gamma}z$  with  $\dot{\gamma}$  the shear rate, and the variance of

the displacement,  $\sigma_{\Delta x}$  were obtained (*cf.* Fig. 1).

In Fig. 2(a), the normalised streamwise dispersion coefficients,  $\mathcal{D}_x = \sigma_{\Delta x}^2/(2\tau)$ , are shown as a function of the delay time  $\tau$ . The variance along the streamwise direction, indicated in Figure 1(b), is  $\sigma_{\Delta x}^2 = \langle (\Delta x - \langle \Delta x \rangle)^2 \rangle$ . Here  $\Delta x(\tau) = x(t + \tau) - x(t)$  is the displacement, and  $t$  the time at which a particle is first observed; we note in particular that we do not use sliding averages due to the non-equilibrium nature of the experiment. In Fig. 2(a),  $\mathcal{D}_x$  has been normalised by the experimental averaged transverse diffusion coefficient  $\bar{D}_y = \langle \sigma_{\Delta y}(z) \rangle / (2\tau)$ , and by the squared shear rate, as in Ref [45]. At least five shear rates are used for each condition. Remarkably, we note a strong modification in the dispersion coefficient on changing the salt concentration: the data for the highest salt concentration gives nearly a three-fold increase in the dispersion, as compared to ultrapure water. Additionally, for pure water, decreasing the laser power gives a further decrease by a factor of 2 between the highest and lowest laser powers employed.

According to the classical Taylor-Aris theory of advection-diffusion, the long-time dispersion coefficient obeys  $\mathcal{D}_x/D_0 - 1 = \text{Pe}^2/30$  for a linear shear flow bounded by reflecting walls [45], where  $D_0$  is the bulk diffusion coefficient of the nanoparticles, and  $\text{Pe} = \dot{\gamma}h^2/(2D_0)$  is the Peclet number comparing advection and diffusion. We note that  $h$  and  $D_0$  are identical for the three different data sets at 150 mW in Fig. 2(a). Therefore, the classical Taylor-Aris theory, supposing non-interacting and finite-sized particles in flows bounded by rigid walls, is clearly inappropriate here. This observation motivates a detailed investigation into the role of the interactions of the nanoparticles with the rigid wall, that of the open boundary, as well as their combined effects on dispersion.

We first note that both the particle and glass surfaces are negatively charged, giving a repulsive interaction that can be modeled via a Debye-Hückel energy potential [12] of the form:

$$U_{el}(z) = kT \frac{a}{\tilde{\ell}_B} \exp\left(-\frac{z-a}{\ell_D}\right). \quad (1)$$

Here  $\ell_D$  is the Debye length,  $\tilde{\ell}_B = e^2/(\epsilon kT) \times [\tanh(e\psi_p/(4kT)) \tanh(e\psi_w/(4kT))]^{-1}$  is a modified Bjerrum length [12], and  $e$ ,  $\epsilon$ ,  $\psi_p$  and  $\psi_w$  are the elementary charge, the dielectric permittivity of the liquid, the particle and wall surface potentials, respectively. At equilibrium, the particles have a Boltzmann distribution, leading to a concentration  $c_B \propto \exp[-U_{el}/(kT)]$ , with  $kT$  the thermal energy.

In Fig. 2(b<sub>i-iii</sub>) are shown the experimental altitude probability distributions (APDs),  $\mathcal{P}$  for identically imposed pressure drops and different salinities; in part (iii) is shown a variation of laser illumination intensity. These distributions are normalised by their maximum values and no filtering concerning the time of observation is made; all particles observed in TIRFM are thus represented and we call these the quasi-equilibrium APDs

(QE-APD) since they are well-described by equilibrium statistics near the wall. Indeed, the lines in Fig. 2(b) are model fits particularly including the Boltzmann distribution,  $c_B(z)$  with the potential given in Eq. (1) as the only energetic contribution — other necessary ingredients described elsewhere in detail [45, 52, 53] include: the finite camera sensitivity giving rise to a large-distance cutoff; and, objective optics and particle polydispersity that modify the direct correspondence between distance and intensity. The good agreement for the full fits here suggests that the electrostatic repulsion mainly [54] determines the distribution of particles near the wall. Quantitatively, the Debye lengths obtained from the QE-APD fits are  $\ell_D = \{67, 32, 10\} \pm 3$  nm for  $[\text{NaCl}] = \{0, 5.4, 54\}$  mg/L, respectively, in agreement with the Debye-Overbeek theory [12]. Furthermore, we find a salinity-independent  $\tilde{\ell}_B = 13 \pm 3$  nm consistent with expected particle and wall potentials of approximately 100 mV. For different salinities, the main effect on the dispersion results is affected through a modified velocity sampling in the depletion regions. Before considering this effect in detail, we qualitatively describe the aforementioned large-distance, camera-sensitivity cutoff.

The observation height,  $h$ , beyond which the camera sensitivity does not allow fluorescence detection, is a key ingredient for the QE-APD fits, and can be tuned by changing the laser power, as shown in Fig. 2(b<sub>iii</sub>). One striking feature of this tunability is to control where a particle's trajectory is no longer considered. Since a particle leaving the observation zone is equivalent to one absorbed, the open boundary acts as an ideal particle sink. Such a sink is expected to modify the probability distribution of particles in the observation zone [4, 33], and thus the particle dispersion, as a depletion of particles near the sink builds up.

In Fig. 3(a), experimental *time-dependent* (TD-)APDs are shown for pure water [55], displaying different delay times since the particles' first observation. As the typical time scale to diffuse out of the observation zone is given by  $h^2/D_0$ , the TD-APDs are plotted for different values of the dimensionless time  $D_0\tau/h^2$ . A temporal evolution of the TD-APD is observed, and a remarkable long-time steady-state is reached for times approaching the diffusion time  $h^2/(D_0\pi^2)$  predicted by Taylor [1]. This long-time, steady distribution is crucially different from the QE-APD shown in black for comparison. We verified that the steady, long-time distribution does not depend on the initial distribution.

We now turn to a theoretical analysis of the dynamical evolution of the time-dependent APD. Our modelling includes both conservative surface interactions and particle consumption, as well as the finite size of the particles through  $z$ -dependent mobilities. We consider a population of nanoparticles initially located at the origin  $x = 0$  (see Fig. 1) and distributed vertically with an initial concentration profile  $c(x = 0, z, t = 0) = c_{\text{ini}}(z)\delta(x)$ . The space- and time-dependent concentration field  $c(x, z, t)$  follows the advection-diffusion equation under external

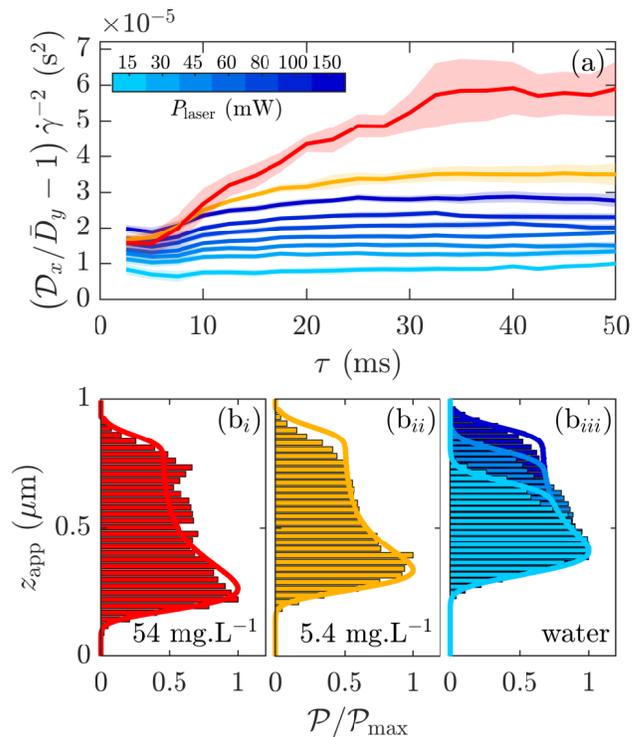


Figure 2. (a) Time dependence of the rescaled particle dispersion coefficient, normalised by the squared shear rate. Each line corresponds to an average over at least 5 different shear rates, the shaded area displaying the associated standard deviation. (b) Normalized quasi-equilibrium altitude probability distributions (QE-APDs) of the apparent distance  $z_{\text{app}}$  between the center of mass of the particle and the glass surface, for varying salt concentrations: (i)  $[\text{NaCl}] = 54$  mg/L (red), (ii)  $[\text{NaCl}] = 5.4$  mg/L (yellow), and (iii) ultrapure water (blue). In (b<sub>iii</sub>), the laser power of the TIRFM is indicated with the shade of blue (only three examples are shown for clarity). The same color code is used in (a).

forcing [28]:

$$\frac{\partial c}{\partial t} + v_x(z) \frac{\partial c}{\partial x} = D_x(z) \frac{\partial^2 c}{\partial x^2} + \frac{\partial}{\partial z} \left( D_z(z) \left[ \frac{\partial c}{\partial z} + \frac{U'_{\text{el}}(z)}{kT} c \right] \right), \quad (2)$$

where  $D_x$  and  $D_z$  are the streamwise and cross-stream diffusion coefficients, reflecting the modification of the particles' altered mobility due to the no-slip boundary condition at the hard wall (see SI). The particle flux vanishes at the wall, imposing the boundary condition  $D_z \left[ \frac{\partial c}{\partial z} + \frac{U'_{\text{el}}(z)}{kT} c \right] = 0$  at  $z = a$ . As nanoparticles are no longer followed after they leave the observation zone the concentration field vanishes at the open boundary, *i.e.*  $c(x, z, t) = 0$  at  $z = h$ . Such a Dirichlet boundary condition is equivalent to a localized first-order chemical (or absorption) reaction with an infinite reaction rate [20].

There are multiple methods available in the literature in order to derive the moments of the concentration field described by Eq. (2), including: the moment theory [46–50], invariant manifold methods [27, 56], Green-Kubo for-

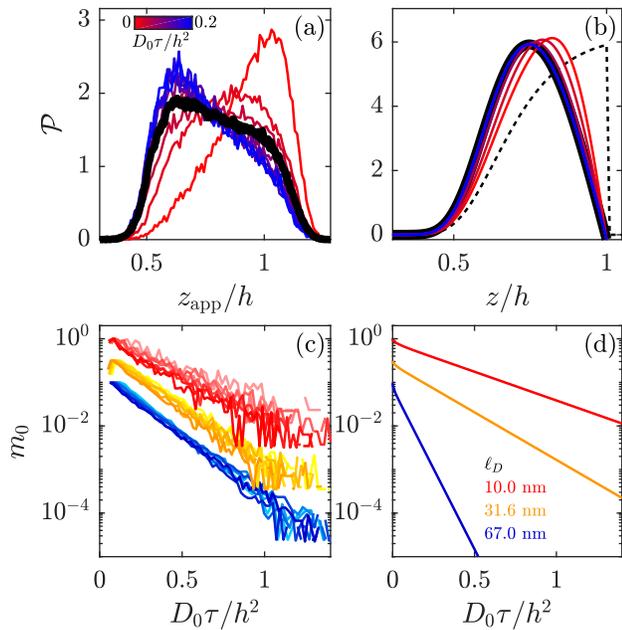


Figure 3. (a) Rescaled experimental altitude probability distributions, for different dimensionless lag times (since the first observation), as indicated in the legend. Here, the liquid is ultrapure water, the laser power is 150 mW and the pressure drop is 30 mbar. The black curve shows the steady distribution (as in Fig. 2(b<sub>iii</sub>)). (b) Theoretical counterpart of (a), with  $2 \times 10^{-3} \leq D_0\tau/h^2 \leq 2 \times 10^{-1}$ . The dashed line corresponds to a Boltzmann distribution  $c_B \propto \exp[-U_{el}/(kT)]$ , with Eq. (1) and the parameters obtained through fitting in Fig. 2(b), that is set as an initial condition in the theory. (c-d) Experimental (c) and theoretical (d) fractions of particles remaining in the observation zone, as functions of dimensionless lag time, for the three salinities used in the experiments. The color code for ultrapure water at various laser powers is the same as in Fig. 2, and shades of red (resp. yellow) indicate the same varying laser power for a  $[\text{NaCl}] = 54$  mg/L (resp.  $[\text{NaCl}] = 5.4$  mg/L) concentration. The curves for different salinities (with Debye lengths as indicated in the legend) are shifted vertically for clarity.

mula [31, 57], and large-deviation theory [58, 59]. Here, we use a moment theory that involves computing the time-dependent streamwise  $p^{\text{th}}$  (with  $p \geq 0$ ) moments  $c_p(z, t) = \int_{\mathbb{R}} x^p c(x, z, t) dx$  recursively; *here and for the following, details are provided in the SI*. Using a modal decomposition, the solution is found to be of the form:

$$c_p(z, t) = \sum_{k=1}^{\infty} c_{p,k}(z, t) \exp(-\lambda_k t), \quad (3)$$

where  $c_{p,k}$  are polynomial functions of  $t$  of degree  $p$ , and  $\lambda_k$  are the eigenvalues of the corresponding Sturm-Liouville problem, with  $\lambda_1 < \lambda_2 < \dots$ . We show in Fig. 3(b) the theoretical APD at different times for an ensemble of particles initially distributed according to a Boltzmann weight,  $c_{\text{ini}}(z) = c_B(z)$  using the same electrostatic parameters and the same  $h$  with an absorbing

top wall as obtained by fitting in Fig. 2(b). We recover the main qualitative features of the experimental observations: (i) a depletion zone develops near the open boundary; and (ii) the TD-APD converges towards a steady distribution at long times, corresponding to the spatial structure of the slowest eigenmode (see SI).

Importantly, the slowest eigenmode has a nonzero eigenvalue  $\lambda_1$ , which means, in particular, that the total number of particles,  $m_0$ , decays exponentially in time at long times. This is a consequence of the non-equilibrium features of the system, and in particular the absorbing boundary condition at the limit of the observation zone. In Fig. 3(c), we show the experimental fraction  $m_0(t) = \int_a^h c_0(z, t) dz / \left[ \int_a^h c_0(z, 0) dz \right]$  of particles remaining in the observation zone, as a function of the dimensionless lag time. No matter the strength of the electrostatic interactions and the laser power, a temporally exponential decay of the number of particles is observed at long times. Similarly, in Fig. 3(d), we show the theoretical fraction of particles remaining in the observation zone, as a function of the dimensionless lag time, for the three Debye lengths found by fitting in Fig. 2(b). As expected, we find once again an exponential decay at large times. This behaviour is set by the smallest eigenvalue  $\lambda_1$ , through  $m_0 \propto \exp(-\lambda_1 \tau)$ , and does not depend on the initial concentration profile of the particles.

From a microscopic point of view, the nanoparticles diffuse out of the observation zone, such that the typical decay time scale is set by the time  $\sim h^2/D_0$  needed for the particle to reach the absorbing boundary at the top of the observation zone. Besides, the decay time also depends in a non-trivial manner on the electrostatic and hydrodynamic interactions via the ratios between the typical length scales in the problem and the channel size. Altogether, the theoretical decay rate reads  $\lambda_1 = \frac{D_0}{h^2} F\left(\frac{\ell_D}{h}, \frac{\tilde{\ell}_B}{h}, \frac{a}{h}\right)$ , where  $F$  is an unknown dimensionless function to be determined by solving the eigenvalue problem described in the SI. In Fig. 4(a), we compare experiments and theory for the dimensionless decay time  $D_0/(\lambda_1 h^2)$  as a function of the Debye-length-to-channel-size ratio. As expected, the stronger the electrostatic repulsion from the wall (*i.e.* the larger Debye length), the faster the particles leave the observation zone. While we note that there is a small-but-systematic deviation between the measured time constants and the predictions of the moment theory, especially for the unmodified water (blue), the overall trend between the two is in agreement.

Taylor-Aris dispersion arises from a particle's continuous sampling of different velocities through its diffusion along the velocity gradients. Since the open boundary of our experiments affects the TD-APDs, as described in Figs. 3(a,b) and as dictated by the spatial structure of the slowest eigenmode, our theoretical approach allows a prediction regarding dispersion. Indeed, computing the first and second moments of the concentration, we are able to extract the dispersion coefficient of the particles remain-

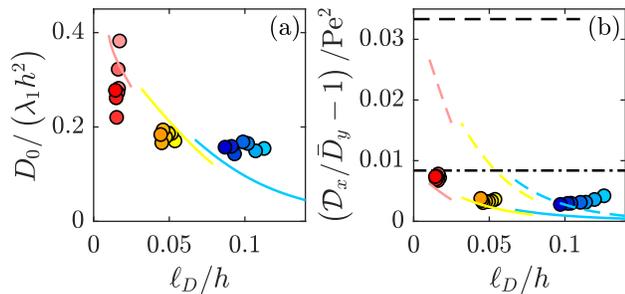


Figure 4. (a) Dimensionless decay time of the number of particles in the observation zone as a function of the ratio between the Debye length and the size of the observation zone. The salinity and laser power is indicated with the same color code as in Fig. 3. The theoretical prediction with an absorbing boundary condition (see SI) is displayed with solid lines. (b) Dimensionless reduced long-term dispersion coefficient as a function of the ratio between the Debye length and the size of the observation zone. The theoretical predictions with an absorbing boundary condition along with electrostatic and hydrodynamic interactions (see Eq. (4)) are displayed using solid colored lines. Also shown are: (black dashed line) the Taylor-Aris prediction; (dashed colored lines) predictions for a closed channel with one reflecting boundary condition [28] (SI) and one wall with electrostatic and hydrodynamic interactions; (black dashed-dot line) the non-interacting tracer-particle model with one open boundary. In the SM Figure S1, all models are schematically described.

ing in the observation zone. This coefficient is found to converge towards a steady value at long times, consistent with the observations in Fig. 2(a). The long-term dispersion coefficient  $D_x$  can be written as the sum of the steady-state averaged streamwise molecular diffusion coefficient  $\langle D_x \rangle$  and a term induced by the advection-diffusion coupling, as follows:

$$D_x = \langle D_x \rangle + \int_a^h \frac{1}{c_B(z)} [v_x(z) - \langle V \rangle] \zeta_1(z) f_1(z) dz, \quad (4)$$

where  $\langle V \rangle$  and  $f_1(z)$  are the steady-state averaged velocity, and the steady TD-APD shown in Fig. 3(b), respectively. The quantity  $\zeta_1$  is an auxiliary function related to the steady-state first moment of the distribution (see SI).

In Fig. 4(b) are shown the rescaled, long-term dispersion coefficients for all of the salinities and laser powers accessed in the experiments. In addition, we display the predictions of Eq. (4) and of the theory in Refs. [28, 31] in the case of a reflecting boundary condition at  $z = h$ . The dispersion coefficient for this latter reflecting case reads  $D_x = \bar{D}_x + f[D_z(z), c_B(z), v_x(z)]$  where  $f$  is a functional (details in SI) depending in particular only on the APD given by  $c_B(z)$  and not on any other distribution. Lastly, we show the case for non-interacting tracer-particles with

one open boundary, not depending on the salt concentration (black dashed-dot line). The reduction of the dispersion coefficient with increasing electrostatic repulsion observed in experiments is well described by the present model (solid colored lines), while we note once again a small systematic deviation that is strongest for the pure water case. Furthermore, Fig. 4(b) stresses that an absorbing boundary condition at the limit of the observation zone is necessary to accurately estimate the dispersion coefficient measured in the TIRFM experiments, and thus that chemically-induced or absorption-induced leakage at boundaries is crucial for describing dispersion at the nanoscale.

In conclusion, we have experimentally and theoretically studied the transport of an ensemble of finite-sized charged nanoparticles near charged surfaces and within an externally-imposed shear flow. In the experiment, the nanoparticles are detected using total-internal-reflection-fluorescence microscopy (TIRFM) in a finite-extent observation zone. In particular, our setup allows us to investigate the importance on the dispersion efficiency of both a repulsive electrostatic interaction with a wall, and an effective absorption at the open boundary of the observation zone. Supported by the moment theory, we show that: (i) the number of particles is not conserved and decays exponentially because of the absorbing boundary; (ii) a steady-state out-of-equilibrium probability distribution of the distance to the wall is reached at long times, with a dynamically-driven depletion zone near the absorbing boundary; (iii) the dispersion coefficient largely depends on the repulsive electrostatic interaction, and is dictated by the steady-state distribution. In our system, with the accessed experimental parameters, the dispersion coefficient appears to be an order of magnitude smaller than the Taylor-Aris prediction. Therefore, at the nanoscale, a precise description of the interactions of the transported entities with the boundaries is essential to fully understand and control of the dispersion. The results given here have clear implications for drug delivery, confined chemistry, or biological processing.

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