Long-range repulsion of colloids driven by ion exchange and diffusiophoresis

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Edited by Monica Olvera de la Cruz, Northwestern University, Evanston, IL, and approved March 12, 2014 (received for review December 10, 2013)

Interactions between surfaces and particles in aqueous suspension are usually limited to distances smaller than 1 \textmu m. However, in a range of studies from different disciplines, repulsion of particles has been observed over distances of up to hundreds of micrometers, in the absence of any additional external fields. Although a range of hypotheses have been suggested to account for such behavior, the physical mechanisms responsible for the phenomenon still remain unclear. To identify and isolate these mechanisms, we perform detailed experiments on a well-defined experimental system, using a setup that minimizes the effects of gravity and convection. Our experiments clearly indicate that the observed long-range repulsion is driven by a combination of ion exchange, ion diffusion, and diffusiophoresis. We develop a simple model that accounts for our data; this description is expected to be directly applicable to a wide range of systems exhibiting similar long-range forces.

\textbf{Exclusion zone (EZ) formation} is a phenomenon where colloidal particles in an aqueous suspension are repelled from an interface over distances of up to hundreds of micrometers, leading to the formation of a particle-free zone in the vicinity of the interface. Such peculiar behavior has been observed by researchers from different disciplines for a wide range of materials, including biological tissues such as rabbit cornea (1), white blood cells (2), polymer gels (3), ion-exchange membranes (4), or metals (5). Depending on the field of research, different terms have been used to refer to the behavior. In biological systems, already in the early 1970s, EZs observed close to the surface of biological tissues such as stratum corneum were referred to as unstirred layers (1), as these colloidal-free layers persisted even when the suspensions were stirred. In later studies, the formation of similar EZs, where Indian ink particles were excluded from the vicinity of leukocyte cells (2), was referred to as aureole formation.

The observed EZ formation is highly surprising, as the forces acting on the colloidal particles can extend over distances of hundreds of micrometers (1–5). Long-range interactions acting on colloidal particles are generally of electrostatic nature (6, 7), with a range set by the thickness of the electrical double layer surrounding a charged colloidal particle, the Debye length \( \lambda_D \). Whereas in low-polar solvents, these electrostatic interactions can act over tens of micrometers (8), in aqueous suspensions these forces are limited to length scales of typically less than 1 \textmu m (6, 7).

A range of hypotheses have been formulated to account for EZ formation, including the emergence of excited coherent vibration modes of molecules in the membrane or the surrounding water that could create large dipole oscillations (9). Deryagin offered a similar explanation, by attributing the aureole formation around cells to long-range forces originating from electromagnetic vibrations; he also mentioned as a possible explanation forces of a diffusiophoretic nature arising in the presence of an electrolyte concentration gradient, but dismissed these in favor of the electromagnetic vibration hypothesis (10). Recently, a chemotaxis hypothesis similar to diffusiophoresis has been suggested and theoretically investigated to account for the EZ formation (11, 12). Effects assuming a long-range structuring of water near hydrophilic surfaces have also been suggested as a possible origin of the behavior (3–5). However, to date it is still unclear whether any of these hypotheses, individually or in combination, can fully account for the observed behavior, as existing comparisons between experiments and theoretical predictions are still unable to clearly discern between the different hypotheses. An understanding of the physical origins of EZ formation is thus still lacking.

In this paper, we study EZ formation in detail by measuring the time and position dependence of forces acting on the particles in multiple configurations. Our experimental results enable us to clearly identify a physical explanation for this intriguing phenomenon, which we expect to apply also to a wide range of other systems exhibiting similar long-range repulsion. To rationalize the observed behavior, we develop a simple model that quantitatively accounts for our experimental data.

\textbf{Results}

To systematically elucidate the EZ phenomenon, we choose the perfluorinated polymer membrane material Nafion 117 as a model system, as EZ formation around this material has already been widely studied (4). Moreover, the material’s physical and chemical properties have been characterized in detail (13, 14) due its widespread use as a proton-conducting membrane in polymer fuel cells (13, 14) and other electrochemical applications, where it is used in the production of NaOH, KOH, and Cl\textsubscript{2} (14). As a colloidal suspension we use uniformly sized polystyrene particles in aqueous solutions of monovalent salt, providing well-controlled and simple experimental conditions.

Although the origin of the force driving the EZ formation is still unclear, particles generally migrate away from the surface, suggesting the existence of a force perpendicular to the surface, acting on the particles. To study this driving force in detail, we

\textbf{Significance}

The ability to displace particles or solutes relative to a background liquid is of central importance to technologies such as filtration/separation, chromatography, and water purification. Such behavior is observed in so-called exclusion zone formation, an effect where particles are pushed away from a surface over long distances of up to hundreds of micrometers. However, it is still unclear which physical mechanisms are responsible. Our work provides a detailed understanding of this exclusion zone formation, enabling a precise control of the behavior. This could be exploited, for instance, for sorting in microfluidic devices, in advanced antifouling coatings, or for elucidating biological processes where it is likely to play an important, yet unexplored role.

Author contributions: D.F. and H.M.W. conceived and designed the experiments; D.F., S.M., J.M.R.H., and H.M.W. designed research; D.F. performed research; D.F. and H.M.W. analyzed data; and D.F. and H.M.W. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1322857111/-\textbackslash dcsupplemental.

www.pnas.org/cgi/doi/10.1073/pnas.1322857111

6554–6559 | PNAS | May 6, 2014 | vol. 111 | no. 18

6554–6559 | PNAS | May 6, 2014 | vol. 111 | no. 18
wish to isolate its effects from those of other forces acting on the particles, such as those induced by gravity or by advection of the suspension. Previous studies of the EZ phenomenon have always used a horizontal setup, where the driving force is perpendicular to the gravitational force, which can lead to the buildup of complex flow patterns (15), an effect that becomes even more pronounced in a setup with Nafion at the bottom, as shown in Movie S1. This has made it difficult to isolate the effects of the formation of EZ on EZ formation, thus preventing a detailed analysis of the kinetics of the process.

To circumvent these problems, we perform experiments in a vertical sample cell, where the Nafion material is placed at the top. This ensures that all forces acting on the particles point in the same direction. We thus expect that particle motion in the system occurs along purely vertical trajectories that are perpendicular to the Nafion surface; this enables us to readily subtract the effects of gravity, thereby isolating the effects of the force that is induced by the Nafion surface. We therefore choose this geometry as our standard experimental setup to study the kinetics of diffusion zone formation. The EZ remains horizontal, as shown for a typical experiment in the sequence of microscopy images displayed in Fig. 1 A–C. To follow the kinetics of the process in detail, we take snapshots of the sample every 5 s. As explained in Materials and Methods, we compose a time–space diagram from these acquired images (Fig. 1D), capturing the development of the EZ profile as a function of time.

This diagram enables us to readily extract the distance \( d_{EZ}(t) \) from the Nafion surface to the edge of the EZ, which we plot in Fig. 1E as red circles. From a separate experiment without Nafion surface we extract the speed of sedimentation of the particles solely due to gravity. As expected, the sedimented distances from the top of the cell, shown in Fig. 1E as green diamonds, are considerably smaller than for the system where Nafion is present (SI Text). To isolate the effects of the force \( F_{EZ} \), we subtract the gravity-induced particle displacement from the observed EZ distance, shown in Fig. 1E as blue squares. Initially, the displacement of particles proceeds rapidly, with a typical velocity of 0.9 \( \mu \)m/s, 300 s after first contact of the suspension with the Nafion surface. The speed of the particles at the edge of the EZ then decreases continuously as time progresses, reaching a typical value of 0.29 \( \mu \)m/s after 1 h.

When plotting \( d_{EZ}(t) \) in a double-logarithmic plot, we observe a simple power-law scaling with slope of 1/2, as shown in Fig. 1F. As expected, the motion only due to gravity, shown as green diamonds, exhibits a purely linear behavior, corresponding to a slope of unity. The simple square-root-of-time scaling of \( d_{EZ}(t) \) is highly reproducible, as illustrated by Fig. 1G, where we display results from five independent experiments performed for particles in an aqueous solution of 1 mM NaCl. The data coincide almost perfectly, as captured by the average of these five independent experiments and the corresponding SDs, presented in Fig. 1H. In fact, we observe a square-root-of-time scaling in all our experiments, independent of suspension properties such as the concentrations and types of salt or colloidal particles used. Moreover, our experiments also indicate that the force \( F_{EZ} \) is not significantly affected by parameters such as the illumination, the thickness of the Nafion layer inside the capillary, or by artifacts such as bubble formation near the surface or irregularities in the shape of the interface (Figs. S1 and S2 and SI Text). The observed square-root-of-time dependence thus appears to be a remarkably robust feature of the EZ formation process.

This scaling indicates that a diffusive process is important in determining EZ formation. Motivated by this observation, we extract an effective diffusion coefficient from the data in Fig. 1E, yielding a value of \( D_{eff} = 1.26 \times 10^{-5} \text{ cm}^2/\text{s} \); this is orders of magnitude larger than the diffusion coefficient expected for our particles in water, as obtained from the Stokes–Einstein relation, \( D_p = k_B T / 6 \pi \eta r \), where \( \eta = 0.001 \text{ Pa} \text{s} \) is the viscosity of water, \( r = 0.5 \mu \text{m} \) the particle radius, \( k_B \) the Boltzmann constant, and \( T = 298 \text{ K} \) the ambient temperature. However, the value of \( D_{eff} \) is within the range of typical diffusion coefficients of monovalent ions in aqueous solution, with typical values ranging from 1.03 \( \times 10^{-5} \text{ cm}^2/\text{s} \) for Li\(^+\) ions to 9.31 \( \times 10^{-5} \text{ cm}^2/\text{s} \) for H\(^+\). This suggests that the physical mechanism that governs EZ formation is directly related to the diffusion of ions.

In fact, Nafion interacts strongly with ions in aqueous solutions; it is a cation exchange material. When an aqueous solution containing cations comes in contact with Nafion, as a result of a higher affinity of the material for these cations, these ions are replaced with H\(^+\) ions initially bound inside the Nafion (14). This ion-exchange process will thus lead to an inhomogeneous distribution of ions in the liquid. As a result, a time-dependent
concentration profile should develop for each ionic species. We hypothesize that this inhomogeneous ion distribution is directly related to the process of EZ formation and the corresponding force $F_{EZ}$ acting on the particles.

Indeed, there is a physical mechanism that results in a drift of particles in liquids with inhomogeneous ion concentrations. This effect, termed diffusiophoresis, was first theoretically described by Derjaguin et al. (16) and later confirmed and studied in more detail both experimentally (17, 18) and theoretically (19–21); the theoretical description of diffusiophoresis is in excellent agreement with experiments, as recently illustrated by a study using microfluidic coflow devices (18).

To obtain an intuitive understanding of this effect, we consider a charged particle immersed in an electrolyte solution with a salt gradient $VC$, as shown schematically in Fig. 2A. The concentration of excess counterions decays with distance from the surface as $C_+ = C_{+0} \exp^{-\lambda D / \lambda D}$, where the Debye length $\lambda_D$ scales with salt concentration approximately as $\lambda_D \propto C^{-1/2}$. As a result, the presence of a salt gradient $VC$ also implies a variation of the Debye screening length along the particle surface, as shown in a schematic close-up of the particle surface region in Fig. 2B.

Within the Debye layer, any small subvolume of fluid contains an excess of counterions and thus possesses a net charge. As a result, each subvolume experiences electrostatic forces under the influence of the local electric field. For a uniform Debye length, the charge distribution around the particle is spherically symmetric, and the resulting stresses occurring in the fluid can be fully balanced by hydrostatic pressure. However, in the presence of a salt gradient, this is no longer the case; the counterion cloud around the particle is anisotropic, with $\lambda_D$ decreasing toward the higher salt concentrations. The corresponding asymmetry of the charge distribution leads to both a gradient in the hydrostatic pressure and nonzero components of the local electric field tangential to the particle surface, as schematically shown in Fig. 2B. Both these effects lead to stresses in the fluid tangential to the surface that cannot be balanced by hydrostatic pressure, thus leading to a flow of fluid along the surface of the particle, generally toward the direction of lower salt concentration. As the overall system is incompressible, this flow must be balanced by a corresponding motion of the particle in the opposite direction (19, 21), as shown schematically in Fig. 2C. Detailed theoretical calculations, taking into account the balance between the hydrostatic pressure and the electrostatic stress (19), result in a constant particle velocity $U$, proportional to the gradient of the logarithm of the ionic concentration $\log C$, as

$$U = D_{DP} \nu \log C,$$

where $D_{DP}$ is the so-called diffusiophoresis constant that depends on the (average) Debye length $\lambda_D$, the zeta potential $\zeta$, the viscosity $\eta$, the temperature $T$, and the diffusion coefficients $D_e$ and $D_a$ of the cations and the anions, respectively (17, 19, 21). If indeed diffusiophoresis is the physical mechanism responsible for the observed EZ formation, then the particle velocities and thus also the velocity of the edge of the EZ should always remain proportional to $\log C$.

To test our hypothesis of diffusiophoresis as the underlying mechanism leading to EZ formation, we thus wish to predict the concentration profile of ionic species in the system as a function of time. In doing so, we consciously neglect some of the rich properties of Nafion, where effects such as interdiffusion of species inside the material (22), swelling behavior (23), or microstructural changes during hydration (13) are known to occur. We focus instead on the well-known ion-exchange properties of the material (14) and assume that the material acts as a perfect drain for cations, where all cations that come in contact with the material are exchanged for $H^+$ ions. The concentration of exchangeable protons within the Nafion material is on the order of 4 M (14), far exceeding the cation concentrations used in our samples. We thus expect that the ion exchange is limited purely by diffusion, rather than by the availability of protons in the Nafion material (24). The problem of predicting the ion concentration profiles thus reduces to solving a set of coupled diffusion equations for all of the involved ionic species under these particular boundary conditions. Whereas the diffusion equation is readily solved for the case of a single electrolyte, for the case of multiple electrolytes, the diffusion problem is difficult to solve analytically. It is known that the diffusion of one species is strongly affected by the presence of others (25); to correctly describe the process we thus need to account for the diffusion of all four ionic species present in the solution ($X^+$, $Y^-$, $H^+$, and $\text{OH}^-$).

For each of these ionic species we can write a Nernst–Planck equation, yielding a system of four coupled equations. However, local electroneutrality and the chemical equilibrium of water ($\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$) reduce these four equations to an analytically tractable system of just two equations for the two electrolytes ($XY$ and $HY$) (25), as

$$\frac{dC_i}{dt} = \sum_{j=1}^{N} D_{ij} \nabla^2 C_i,$$

where the $D_{ij}$ is the matrix of diffusivity coefficients for the electrolytes that can be obtained experimentally (25, 26) but also can be theoretically approximated (26). This treatment considers the concentration profiles of the two electrolytes rather than those of the separate ions, thus implicitly satisfying charge neutrality. As explained in more detail in SI Text, it has been shown that a system of this kind can be solved analytically, yielding a solution for the concentration $C_i(x,t)$ of the simplified form

$$C_i(x,t) = f_i(C_{\text{initial}}, D_{ij}, F(D_i,x,t)),$$

where $C_{\text{initial}}(x,t)$ is the initial concentration of electrolytes, and $F(D_i,x,t)$ is the solution for the binary case for the given boundary conditions (27). This solution thus yields detailed predictions for the ion concentration profiles.

We plot in Fig. 3A the resulting ion concentrations for a 1-mM NaCl solution at a time $t = 300$ s. As prescribed by the boundary
conditions, the concentration of NaCl (red circles) vanishes close to the interface and increases with increasing distance from the surface, reaching a plateau at a distance of several millimeters. Conversely, the concentration of HCl (blue squares) exhibits a plateau at small separation distances, whereas with increasing separation it decreases toward zero. The total electrolyte concentration profile, derived by adding these two profiles, exhibits a distinct maximum. This can be explained by the fact that the flux of HCl from the surface has to match the flux of NaCl to the surface; however, HCl diffuses faster than NaCl, thus leading to a region of lower total electrolyte concentration near the surface and a corresponding region of increased electrolyte concentration farther away from the surface, which is required to conserve the total number of electrolytes in the solution.

If EZ formation is indeed governed by diffusiophoresis, then particles should migrate at a velocity proportional to the calculated Vlog C. To test this hypothesis, we consider the particles at the edge of the EZ, for which we can readily extract the position dEZ directly from our experiments. The corresponding particle velocities U(dEZ(t), t) should then be directly proportional to the calculated Vlog C at the same position and time.

Indeed, when plotting the experimental U(dEZ(t), t) as a function of the calculated Vlog C, we find an almost perfectly linear behavior, as shown in Fig. 3B for a system of polystyrene particles in a 1-mM NaCl solution. This behavior is in full agreement with our hypothesis of diffusiophoresis; we thus interpret the slope of this curve as the diffusiophoresis coefficient, determined by a linear fit as DP = 2.81 × 10⁻⁵ cm²/s.

Our experiments show that the EZ formation exhibits a robust square-root-of-time dependence. This is in fact a direct consequence of the scaling properties of the time-dependent salt concentration profile C(x, t). The time evolution of C(x, t) is governed by diffusion, any characteristic length scales in the profile have to scale with the square root of time. Further, as the boundary conditions at x = 0 and x = ∞ are fixed, its magnitude remains unchanged. To illustrate this scaling (full analysis in SI Text), we plot the calculated C(x, t) for different times t as a function of x√t, resulting in a single master curve, plotted in Fig. 3C. This shows that for all times t, the concentration profile is given by C(x, t) = C(x/√t0, t0), where t0 is an arbitrary reference time. Similarly, the gradient of the profile is obtained directly from the gradient at a reference time t0 as ∇log C(x, t) = √t0/∇log C(x/√t0, t0), as shown by the master curve shown in Fig. 3D. In our experiments we have observed dEZ = a√t and thus dEZ = a/2√t. The scaling properties of C(x, t) also imply that Vlog C (dEZ(t), t) = const./√t, thus predicting that the diffusiophoresis condition dEZ = DP Vlog C is fulfilled for particles at the edge of the EZ. The diffusiophoresis coefficient DP can thus be directly obtained from the magnitude a of the EZ trajectory as

\[ DP = \frac{a}{2\sqrt{t_0}\log C(d_{EZ}(t_0), t_0)}. \]  

Particles in front of this trajectory will move slower and particles farther back will move faster, as shown in Fig. 3E, where we plot the predicted trajectories of particles with different starting positions; this leads to the observed accumulation of particles at the edge of the EZ.

The scaling properties of C(x, t) thus enable us to predict the detailed motion of particles and thereby the formation of the EZ, based on a single ion profile, calculated at one single reference time t0, with the diffusiophoresis coefficient DP as the only free parameter. Doing so, we use a simple one-dimensional model to predict the detailed distribution of particles in the sample. In this model, point particles are initially uniformly...
determined and their trajectories are calculated based on the calculated salt concentration profile. To visualize the predictions of this simple model, in analogy to Fig. 1D, we construct a space–time diagram, displayed in Fig. 3F, using the $D_{dp}$ value obtained from Fig. 3B. Comparing this diagram to the experimental diagram shown in Fig. 3G, we observe that the scaling of the edge of the EZ is captured very well, again displaying the characteristic square-root-of-time dependence. However, the edge of the EZ appears much sharper than in the experiment. We attribute this discrepancy to the fact that our simple model does not consider the diffusion of particles or the effects of flow instabilities driven by gradients in particle concentration that are built up during the process (Movie S2).

Our experiments thus show that ion exchange and diffusiophoresis can fully account for the phenomenon of EZ formation. Using a single parameter, the diffusiophoresis coefficient $D_{dp}$, the development of the EZ with time is predicted with high accuracy, as shown in Fig. 3H. However, so far we have not considered the dependence of the diffusiophoresis coefficient on particle and solution properties such as the zeta potential, the Debye screening length, and ionic mobilities (17, 19, 21). To further scrutinize our hypothesis, we thus vary the suspension properties to test whether, as predicted, they affect the dynamics of EZ formation. To do so, we make use of the differences between the ionic mobilities of monovalent Cl$^-$-based electrolytes. We prepare a series of samples containing LiCl, NaCl, KCl, and CsCl where the diffusivity of the cation continuously increases from Li to Cs. As shown in Fig. 4A, whereas in all cases EZ formation still exhibits the characteristic square-root-of-time dependence $d_{EZ} = a\sqrt{t}$, we indeed find a systematic change of the kinetics of EZ formation in this series of samples, as the parameter $a$ decreases consistently with increasing diffusivity of the cations (28). This clearly indicates that the diffusivity of the ions directly affects the kinetics of EZ formation, thus further strengthening our hypothesis.

The diffusiophoresis coefficient should also depend on salt concentration $C$, which affects both the Debye screening length and the zeta potential. To test this, we prepare samples containing different concentrations of NaCl salt, ranging from $C = 1$ mM to $C = 100$ mM. As shown in Fig. 4B, as a function of salt concentration we observe a systematic change in the kinetics of EZ formation, whereas the characteristic square-root-of-time scaling of $d_{EZ}$ with time is again preserved. With increasing $C$ we observe a shift toward lower $d_{EZ}$, corresponding to a decrease of the parameter $a$ that describes the time dependence of the EZ position $d_{EZ} = a\sqrt{t}$.

**Fig. 4.** EZ formation as a function of solution properties. (A) For different monovalent salts with mobilities increasing from LiCl (red circles), NaCl (blue squares), and KCl (green diamonds) to CsCl (black crosses); $C = 1$ mM. (B) $d_{EZ}(t)$ as a function of time for different salt concentrations of NaCl solutions, 1 mM (red circles), 10 mM (blue squares), and 100 mM (green diamonds). The solid lines have a slope of 1/2.

**Conclusions**

We have performed detailed experiments to study the origin of EZ formation. By minimizing the influence of convection and other forces acting on the particles, we isolate the force responsible for the observed long-range interactions. We observe a robust square-root-of-time scaling of the EZ distance, which we link directly to the diffusion of ions in the system. We have used a theoretical description of diffusion in a ternary system with boundary conditions set by the ion-exchange properties of the Nafion material. Comparing this model to the observed particle kinetics, we show that the particle velocity is proportional to $V_{logC}$, the scaling predicted for diffusiophoresis of colloids in a salt gradient. Our force for so-called self-propelled particles (29, 30) or in microfluidic applications to control the distribution of colloids in a channel (18), the effect is still rarely studied or used in applications. However, the effects studied here could have important implications also in biological systems, for instance in the study of biological chemotaxis, where a migration of cells is observed in response to chemical gradients. Diffusiophoresis could also be the nonspecific repellent force creating phagosomes (31) and vacuoles (32) surrounding bacteria (33) or parasites (34–36) attacking or being attacked by living cells. The results of our study suggest other potential applications, as they offer a detailed understanding of how EZ formation can be precisely controlled by tuning the properties of the involved interfaces and solutions. This understanding could be exploited, for instance, for the creation of novel antifouling materials or for the sorting of cells or particles in microfluidic devices.

**Materials and Methods**

**Sample Preparation.** Our basic system consisted of a Nafion 117 membrane (Nafton; Sigma Aldrich) fitted inside a capillary of rectangular cross section (length, 50 mm; width, 4 mm; height, 400 μm; Vitrocom), deionized water (MilliQ; resistivity 18.2 MΩ), uniformly sized polystyrene (PS) beads of 1-μm diameter, and a monovalent salt (Sigma Aldrich). The capillary tubes were fitted at one end with Nafion by stamping the tube for 20 s on a Nafion sheet placed on a glass plate, preheated to 265 °C. This process ensured that the Nafion material uniformly filled and sealed the capillary. To prevent evaporation, the capillary was further sealed using a UV curable glue (Norland 63; Norland Products), which closely matches the refractive index of glass. To prevent optical distortion we placed a second coverslip glass (size 1) on top of the capillary and glue, thereby creating a uniform layer of index-matching materials. The glue was then cured under a UV lamp for 24 h. At the start of an experiment the capillary was filled with a PS suspension, with this moment referred to as the starting time of the experiment. The open end of the capillary was then sealed with a 90-s epoxy (Bison) to prevent evaporation of the solution.

**Imaging.** The final sample cell was imaged in a vertical setup consisting of (i) an XYZ stage used to manipulate the supporting microscope slide, (ii) An
inverted microscope (Zeiss Axiosvert A200 and Motic BA 310) capable of imaging in a vertical geometry by use of an attached microscope objective inverter (Inverted Optocoupler Objective Inverter; LSM TECH) fitted with an objective of 1× magnification, and (iii) a 100-W Olympus lamp in combination with a Motic condenser (N.A. = 0.55, walking distance = 70 mm). The images were recorded using a monochromatic CCD camera (Imaging source, DMK 21AU04, 640 × 480 pixels).

**Digital Image Analysis.** To construct the time–space diagram shown in Fig. 1D, horizontally averaged vertical lines from each frame were combined into a single image. The diagram was then corrected to remove the influence of the flickering of the lamp, inhomogeneous illumination, glass thickness, and differences in optical path length through the setup. EZ trajectories were obtained by digital image analysis, where the position of the Nafion interface was identified as the point where the first derivative of the intensity reached a maximum.

**ACKNOWLEDGMENTS.** We thank Y. Gao, P. Voudouris, Z. Fahimi, P.D. Anderson, J. Mattsson, and V. Trappe for valuable discussions. S.M. gratefully acknowledges financial support from the Stichting voor de Technische Wetenschappen (STW), the technological branch of the Netherlands Organisation of Scientific Research, and the Dutch Ministry of Economic Affairs under Contract 12538, Interfacial effects in ionized media. D.F. and H.M.W. are grateful for financial support from the Institute for Complex Molecular Systems (ICMS) at Eindhoven University of Technology.

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