Evidence of Sequentially Formed Charge Patches Guiding Ions through Nanocapillaries

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We investigated the time evolution of the dynamically shifting distribution of 7 keV Ne^{7+} ions guided through nanocapillaries in SiO_2. We present evidence for a small number of charge patches, formed sequentially in the charging-up process, guiding the ions. We show that the charge patches are distributed along the whole length of the capillaries and that they are maintained in the equilibrium state of transmission. The interpretations are supported by model calculations.

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Advances in the field of nanostructures in recent years made it possible to manufacture membranes with nanosized capillaries in various materials. Nanocapillaries in insulating materials have been used as filters to selectively capture biosized molecules [1]. Thus, the need for tools to characterize the electric properties of nanosized capillaries has emerged. One such tool that has appeared to be possible is the use of slow highly charged ions (HCI) to probe the electrical properties of nanocapillaries of high aspect ratios in insulating materials. Measurements of Stolterfoht *et al.* [2] showed that, in contrast to metallic capillary arrays, there is guiding of slow HCI through a membrane of nanocapillaries in insulating *polyethylene terephthalate* (PET) even when the membrane is tilted a few degrees so that it is not geometrically transparent to the ion beam. This makes it possible to steer the beam by tilting the capillary membrane. There has been much research activity recently, involving different capillary materials, such as PET, SiO_2, and Al_2O_3 [3–10] with typical results that the large majority of the transmitted ions retain their initial charge state and kinetic energy, with angular spreads close to the aspect ratio. It has been suggested that channeling through carbon nanotubes could be used to steer ion beams, although the kinetic energy of the ions would be substantially reduced from many inelastic collisions with carbon atoms [11]. Ions guided through insulating nanocapillaries show no significant energy loss [2,5,6,9], which would, in this respect, make insulating capillaries a better candidate for ion-beam steering.

The guiding phenomenon has been attributed to a self-arranged formation of charge patches on the capillary walls that deflect subsequent ions, inhibiting close collisions with the capillary walls [2–8,12,13]. A model with multiple charge patches located throughout the whole length of the capillaries, with a scattering region at the entrance followed by a guiding region towards the exit, was proposed by Stolterfoht *et al.* [2,3]. Theoretical work consisting of Monte Carlo simulations has explained guiding through PET capillaries with the entrance charge patch as the main deflection point and possibly a second weaker patch further inside the capillaries [12,13]. A distinction between the two different views of guiding in the region downstream of the entrance charge patch has so far not been possible.

In this Letter we present results that clearly show that there is a small number of sequentially formed charge patches, distributed along the length of the capillaries, involved in the guiding. We used very parallel SiO_2 capillaries and high-resolution two-dimensional imaging of transmitted ions. And, with time resolved measurements of the angular distributions during charging-up of the membrane, we have been able to identify unambiguously that single charge patches are building up with time and, one ends up with a small number of patches in the stationary state of transmission. The charge patches are formed on alternating sides in the plane of incidence, resulting in oscillatory ion trajectories similar to, although at a larger scale, the trajectories of ions channelling between crystal planes [14].

The experiments were performed at the Manne Siegbahn Laboratory (MSL) in Stockholm using a beam of 7 keV Ne^{7+} ions from the 14.5 GHz ECR ion source. The beam was collimated by a pair of four-jaw slits, set 1.55 m apart. The beam size was 2×2 mm^2 and the intensity was approximately 5 pA/mm^2 at the membrane. The capillary membrane was mounted on a goniometer allowing independent adjustment in three spatial directions and around two rotational axes. The transmitted ions were detected using microchannel plates with a resistive anode, placed at a distance of 62 cm from the target membrane.

The membrane used in our experiments contains SiO_2 capillaries with diameters of 100 nm and lengths of 25 μm (aspect ratio of 250:1, corresponding to an angular opening of 0.23°) spaced 1.4 μm apart. The capillaries were made by thermally oxidizing pores in a Si membrane to a wall thickness of 100 nm [15]. The geometrical transparency is 0.4% and the capillary density is 5×10^7 cm^{-2}. Both membrane surfaces are layered with 30 nm of gold to prevent macroscopic charging-up. In the experiments the membrane is first oriented in two axes so that the capillaries are aligned with the beam. The angle between the capillary axes and the incident beam is referred to as the tilt angle. The observation angles ϕ and θ are given with respect to the incident beam direction, ϕ is in the same plane as the tilt angle and θ is in a plane perpendicular to the tilt angle. The charging-up experiment at the presented tilt angle of $-2°$ was made after discharging for days, and it was repeated after letting the membrane discharge for three months, while keeping all the settings for the beam alignment and the capillary orientation, and the two series show the same results.

The angular distributions at different times of the charging-up process are shown in Fig. 1, for a tilt angle of $-2°$. After an incident charge of 250 e/cap (elementary charges/single capillary) transmission rate has increased to approximately 0.2% and is centered at 0.6° off the capillary axes [Fig. 1(a)]. After 420 e/cap the distribution is only 0.3° offset from the capillary axes [Fig. 1(b)] and with 1290 e/cap of incident charge, the distribution peak has shifted by an additional $-0.5°$ to the other side of the capillary axes [Fig. 1(c)]. This is a *turning point* from where, with increasing charge deposition, the distribution peak is gradually shifted back to end up being aligned with the capillary axes in the stationary state of transmission [Fig. 1(d)].

A more complete set of transmission profiles, projected onto the ϕ plane are shown in Fig. 2(a), where it is seen how the distribution shifts in the plane of the tilt angle during charging-up. In the θ plane (perpendicular to the plane of incidence), see Fig. 2(b), there is no substantial shift; this is according to expectations, since in this plane the capillary axes are aligned with the beam. Shifts in the transmitted distribution have been observed previously [8–10]. We start, however, from completely discharged capillaries under well-defined conditions and find clear time- and position-correlated shifts from which we can derive a time evolution of distinct charge patterns.

Transmission in the beginning is offset by $+0.6°$ from the capillary axes, towards the incident beam direction [Fig. 1(a)]. This is geometrically impossible if the only point of deflection is at the entrance charge patch. Only when there is a second deflection in the latter half of the capillary length (aspect ratio 100:1) there can be transmission that is offset 0.6°, towards the incident beam direction [Fig. 1(a)]. Only a small fraction, $\approx 0.2\%$, of the ions entering a single capillary are guided through at this stage, leaving the majority of ions to deposit charge when hitting the capillary walls. Why do we not observe ions deflected, in the early stage of charging-up, from the entrance patch? They should be transmitted at angles ranging from alignment with the capillary axes to $-0.26°$ away from the incident beam direction (aspect ratio $\approx$ 200:1). Our reasoning is as follows: the solid angle for scattered ions is small and the time before the second patch is formed is far too short to accumulate enough counts on the detector. Our simulations, which are discussed below, show that somewhat less than half of the ions entering a single capillary are deflected by the entrance charge patch and continue further inside the capillary. Some of these ions build up the second charge patch, while some are deflected and continue further towards the exit, many of which must be hitting the wall close to the exit. These ions will form a third charge patch that deflects exiting ions away from the incident beam direction [Fig. 1(b)]. This patch will, however, not be as localized as the entrance patch, since the preceding deflections also introduce a spread in the

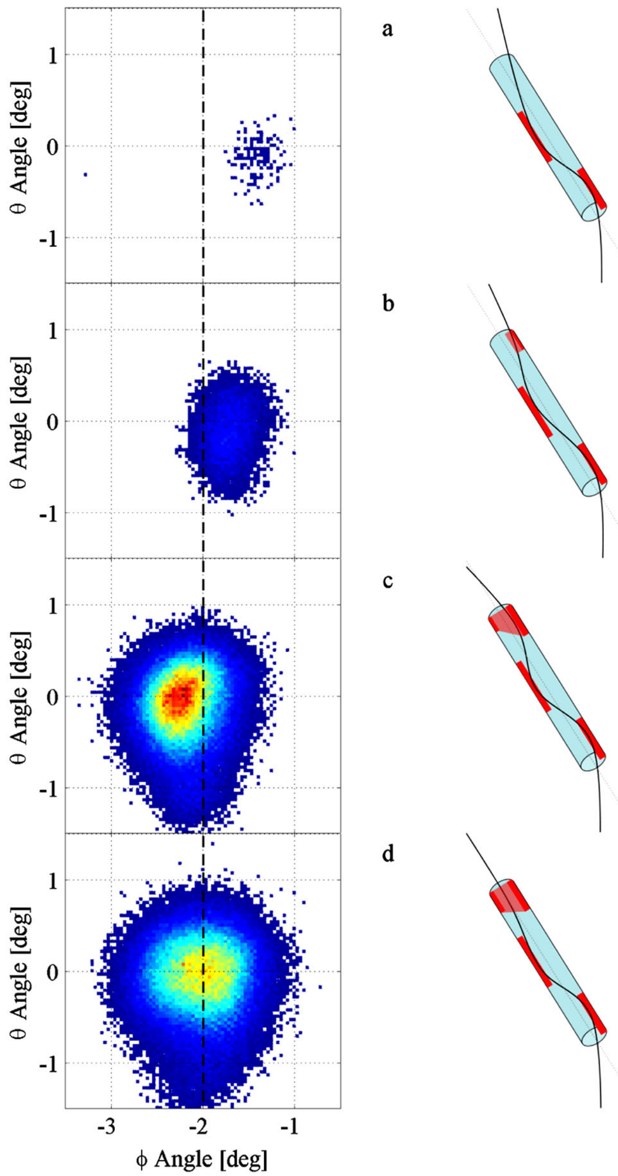

FIG. 1 (color online). (Left) Two-dimensional images after varying amounts of incident charge during charging-up, (a) after 250 e/cap (elementary charges/single capillary), (b) after 420 e/cap, (c) at the turning point, after 1290 e/cap, and (d) after 4360 e/cap. The dashed line indicates the tilt angle. (Right) Schematic drawings of charge patches with corresponding sample trajectories. Dimensions and angles are not to scale.

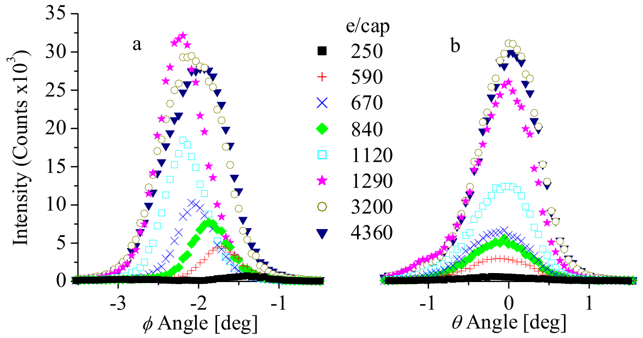

FIG. 2 (color online). Distributions of transmitted ions at various stages of the charging-up process. (a) ϕ-plane projections, (b) θ-plane projections.

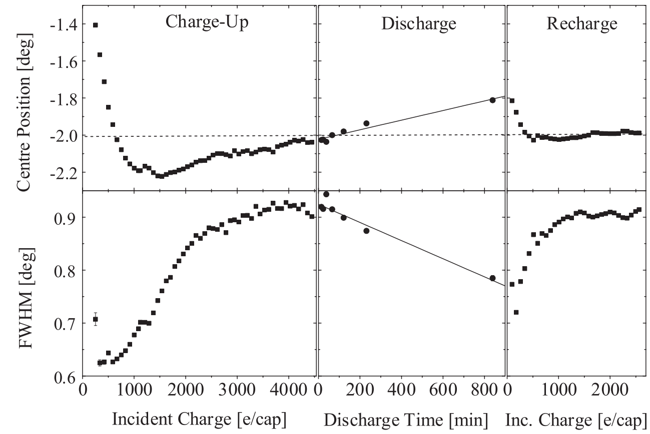

FIG. 3. Projections onto the ϕ plane, peak centers (top), FWHM (bottom), shown for charging-up (left), discharging (middle), and recharging (right). Note that the scale on the abscissa is in units of incident charge for the charging-up and recharging graphs, and in units of time for the discharging graph. The dashed horizontal line indicates the tilt angle; the solid lines are linear fits to the data points.

θ plane. The three charge patches are initially located on alternating sides of the capillary walls in the plane of incidence, resulting in oscillatory ion trajectories. The continuous accumulation of charge in the exit charge patch causes exiting ions to be deflected more and more towards larger observation angles until a turning point is reached, see Fig. 1(c). Around the time the turning point is reached, the exit charge patch has become extended around the circumference of the capillary. This causes a reduction of the transverse electric field at the capillary exit, in the plane of the tilt angle, which results in the shift of the transmitted ion distribution back towards being aligned with the capillary axes, see Fig. 1(d). One could consider a formation with a larger number of charge patches for the beginning transmission, but that would place the last deflection point closer to the exit, allowing for a larger width than what is observed. A larger number of patches in the latter half of the capillaries would imply that there are more turning points in the shift of the distribution, which cannot be seen in the experiment. Therefore, a formation with other than three charge patches at equilibrium is unlikely. The exact number of charge patches for any given experiment is, however, expected to vary with the material properties and dimensions of the capillaries, the tilt angle, and the charge and kinetic energy of the incident ions.

The charging-up measurement was followed by a discharging measurement, which in turn was followed by another charging-up, or rather recharging measurement. In the upper left pane of Fig. 3 we show a plot of the center positions of the distributions and it is obvious that the distribution, initially offset from the orientation of the capillary axes, shifts to a turning point, after which it gradually shifts to become aligned with the capillary axes. The time evolution of the full width at half maximum (FWHM) is shown in the lower left pane of Fig. 3. The FWHM is around 0.6° in the beginning and broadens to 0.9° in the stationary state, while in the θ plane it lies constantly around 0.8°. It has been suggested that the mean field from the entrance charge patches create an inhomogeneous field at the exit that defocus exiting ions, causing a broadening of the distribution [8,12,13]. We made calculations for our SiO_2 capillaries that show that the maximum contribution to the exit angle of ions in such a defocusing field (even if all incident charge were put in the entrance patches) is as small as 0.01°. The starting width of 0.6° is compatible with deflection from the second patch halfway in the capillary (aspect ratio $\approx$ 100:1). The broadening in the ϕ plane is mainly due to the reduction of the collimation by the exit wall as the third charge patch builds up, see Figs. 1(a)–1(d), and confirms the interpretation of the data.

The shift of the centroids during the 14-hour discharging measurement, where transmission was probed by 100 s long pulses, is shown in the upper middle pane of Fig. 3. During discharging, the peak center shifts smoothly from $-2°$ to $-1.8°$, while the total transmission rate goes down by approximately 30%. During recharging it was observed that the distribution smoothly shifted back to again become centered around the capillary axes after only 400 $e/$cap of incident charge; see upper right pane of Fig. 3. Also shown in Fig. 3 is how the width decreases slightly during discharging and rapidly regains its stationary value of 0.9° when the capillaries are being recharged.

A question that arises is whether the charge patches formed in the latter part of the capillaries are maintained as the transmission peak stabilizes around the orientation of the capillary axes, or whether they have a transient character as suggested by previous simulations for PET capillaries [12,13]. The fact that there is no turning point for the shift of the distribution at all for the recharging measurement is proof that the charge patches are maintained when the stationary state of transmission is reached, and only weakened during the 14-hour discharging. Had the charge patches in the latter half of the capillaries been only transiently existing during charging-up, a turning

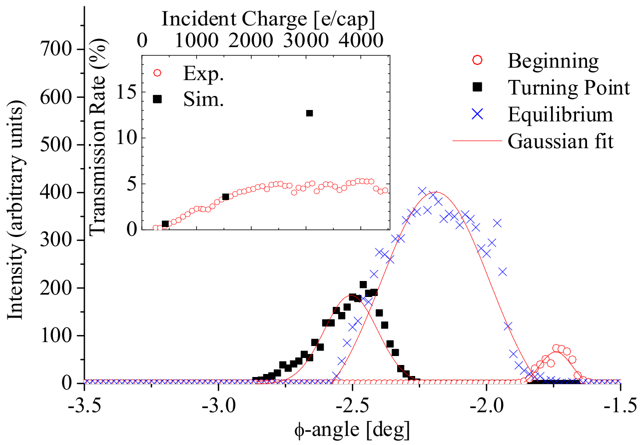

FIG. 4 (color online). Distributions in the ϕ plane from simulation, at three stages of the charging-up process, at the beginning, around the turning point, and close to equilibrium. The inset shows transmission rate per capillary from simulations (solid squares) and from experiment (open circles).

point should be seen also in the recharging experiment as the charge patches were reforming.

To support the conclusions from our observations we have performed model simulations of guiding at the selected tilt angle of $-2°$. We place a varying number of sequentially formed charge patches on the capillary walls, located according to geometrical considerations. The patches are modeled by a planar potential of the form

$$U = U_{\varphi z} e^{-(a-\rho)/a} = U_z \cos^n\left(\frac{\varphi + \varphi_\circ}{2}\right) e^{-(a-\rho)/a},$$

where U_z is the potential along the capillary axes, a is the radius of the capillary, and ρ is the radial displacement of an ion from the center of the capillary, while the cosine term describes the angular distribution of the potential in a plane perpendicular to the capillary axes. The exponential term describes the potential radially and the exponent n is used to vary the degree of localization around the circumference of the capillaries. The potential distribution along the axial dimension is realized by dividing the capillary into short cylindrical regions and assigning them different values of U_z. The model potentials were applied to a representative capillary, through which 10^5 trajectories were simulated for ions initialized by Monte Carlo methods, taking into account the divergence of the beam. Simulations were made for three different stages of the charging-up process, the beginning, around the turning point, and close to equilibrium.

Distributions from the simulations, projected onto the ϕ plane, are shown in Fig. 4 for the three different stages; although the peak centers at $-1.7°$, $-2.5°$, and $-2.2°$ differ slightly from the corresponding experimental peak centers at $-1.7°$, $-2.2°$, and $-2.1°$; the shift is reproduced qualitatively. The widths of $0.2°$–$0.5°$ are narrower than the experimental widths of $0.6°$–$0.9°$. This difference is, in fact, not so large, if we consider that one single capillary was used in the simulations, while in the experiment there are contributions from 2×10^6 capillaries. There are also contributions to the experimentally observed width from a small but not completely negligible spread of the capillary axes (less than $0.2°$). We show in the inset of Fig. 4 the transmission rate per capillary from the simulations, together with the experimentally observed transmission rate and agreement is found to be reasonably good.

In conclusion, we have shown that a small but finite number of charge patches are sequentially formed, which guide the ions through the nanocapillaries. The distribution of transmitted ions shifts in the plane of the tilt angle as the charge patches are building up, indicating oscillatory ion trajectories inside the capillaries. The experimentally observed shift of the distribution is reproduced in simulations of ion trajectories guided by simple model potentials. The findings that a small number of charge patches are formed, and maintained at equilibrium, are an important step towards understanding the mechanisms of guiding through insulating nanocapillaries and is of great importance for future development of ion-beam steering applications employing insulating nanocapillary membranes.

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[1] S. E. Létant, T. W. van Buuren, and L. J. Terminello, Nano Lett. **4**, 1705 (2004).
[2] N. Stolterfoht *et al.*, Phys. Rev. Lett. **88**, 133201 (2002).
[3] R. Hellhammer *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. B **233**, 213 (2005).
[4] Gy. Víkor *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. B **233**, 218 (2005).
[5] M. B. Sahana *et al.*, Phys. Rev. A **73**, 040901(R) (2006).
[6] S. Mátéfi-Tempfli *et al.*, Nanotechnology **17**, 3915 (2006).
[7] P. Skog *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. B **258**, 145 (2007).
[8] N. Stolterfoht *et al.*, Phys. Rev. A **76**, 022712 (2007).
[9] H. F. Krause *et al.*, Phys. Rev. A **75**, 042901 (2007).
[10] Y. Kanai *et al.*, *XXV International Conference on Photonic, Electronic, and Atomic Collisions, Freiburg, Germany; Book of Abstracts*, edited by J. Anton *et al.* (Freiburg, 2007), p. Fr 160.
[11] A. V. Krasheninnikov and K. Nordlund, Phys. Rev. B **71**, 245408 (2005).
[12] K. Schiessl *et al.*, Phys. Rev. A **72**, 062902 (2005).
[13] K. Schiessl *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. B **232**, 228 (2005).
[14] D. S. Gemmel, Rev. Mod. Phys. **46**, 129 (1974).
[15] R. T. R. Kumar *et al.*, Nanotechnology **16**, 1697 (2005).