Electronic Supporting Information

Magnetic field effects dynamics of ethylammonium nitrate ionic liquid confined between glass plates

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Figure S1. Alignment of glass plates with confined EAN.

A chemical composition of glass plates (Thermo Scientific Menzel-Gläser, Menzel

GmbH, Germany)

SiO ₂	64.1%	CaO	
B_2O_3	8.4%	BaO	
Al_2O_3	4.2%	ZnO	5.9%
Na ₂ O	6.4%	TiO_2	4.0%
K_2O	6.9%	As_2O_3	
MgO		Sb_2O_3	0.1%

Cleaning of glass plates. The glass plates were carefully cleaned to achieve the highest possible hydrophilicity of the glass for each experiment. The glass plates were immersed in Extran AP21 (Merck, Darmstadt, Germany) 5% aqueous solution for 1 h, followed by an Extran MA02 (Merck, Darmstadt, Germany) 5% aqueous solution for 1 h with moderate agitation. The glass plates were then washed with MQ water and 99.7% ethanol and kept under vacuum for an hour.

Contact angle measurements. The contact angle was measured using a pocket goniometer (PG-X, FIBRO System AB, Sweden) at room temperature (21 °C) and calculated using the associated software. The liquid was pumped from a reservoir to a needle that squeezes out small uniform drops of a selected size onto the designated substrate. The cleaned glass-plates were rinsed with acetone and dried with N₂ gas prior to use. All contact angles were measured at least twice on both sides of the substrate and on two different surfaces of the substrate. The contact angle was measured using water (Milli-Q) to verify the hydrophobicity of the substrate. The cleaned glass surface had a contact angle near 0°. Preparation of samples (filling with EAN) was performed immediately after the cleaning procedure.

Silanization of glass plates. The glass plates were silanized to increase the hydrophobicity of the glass. Silanization solution 1 (~5% of dimethyldichlorosilane in heptane) from Sigma Aldrich (Germany) was used. The glass plates were washed with 99.7% ethanol before silanization to remove surface impurities and surface water. Traces of ethanol were removed by vacuum pumping at $5 \cdot 10^{-5}$ bar for 3 hours. The silanization

process was performed overnight (14 hours). Unreacted reagent was removed by washing in acetone with subsequent removal of traces of acetone by vacuum pumping. The silanized glass sample had a contact angle between 91° and 96°.



Figure S2. Changes in the diffusion decays (DDs) of the ¹H NMR signals of EA cations recorded at 293 K by pulsed-field-gradient stimulated echo experiments in EAN films confined between parallel polar glass plates, with gradient directions *along* the plates. Diffusion time was 3 ms.



Figure S3. The DDs of the ¹H NMR signals of EA cations recorded at 293 K by pulsed-field-gradient stimulated echo experiments at different diffusion times (t_d) in EAN films confined between parallel polar glass plates, with gradient directions along the plates after placing the sample in the magnetic field of the NMR spectrometer (solid symbols) and after 12 hours (open symbols).



Figure S4. Changes in the DDs of the ¹H NMR signals of EA cations recorded at 293 K by pulsed-field-gradient stimulated echo experiments in EAN films confined between parallel polar glass plates, with gradient directions *perpendicular* to the plates. Diffusion time was 3 ms.



Figure S5. The DDs of the ¹H NMR signals of EA cations recorded at 293 K by pulsedfield-gradient stimulated echo experiments in bulk EAN (solid squares, $D_0 = 3 \cdot 10^{-11} \text{ m}^2/\text{s}$) and in EAN films confined between parallel polar glass plates with gradient directions *perpendicular* to the plates just after placing the sample in the magnetic field of the NMR spectrometer at different diffusion times (t_d). The best fits using Eq.(S2) for restricted diffusion are represented by colored lines corresponding to the data points.



Figure S6. The DDs of the ¹H NMR signals of EA cations recorded at 293 K by pulsedfield-gradient stimulated echo experiments in bulk EAN (dashed line, $D_0 = 3 \cdot 10^{-11} \text{ m}^2/\text{s}$) and in EAN films confined between parallel polar glass plates with gradient directions *perpendicular* to the plates, 12 hours after placing the sample in the magnetic field of the NMR spectrometer. The best fits using Eq.(S2) for restricted diffusion are represented by colored lines corresponding to the data points.



Figure S7. ¹H NMR T_2 relaxation decays for protons of different chemical groups of EA cations in EAN films confined between parallel polar glass plates just after placement in a magnetic field of 9.4 T of the NMR spectrometer. T = 293 K.



Figure S8. Diffusion decays of the ¹H NMR signals of EA cations recorded at 293 K by pulsed-field-gradient stimulated echo experiments with bipolar gradients (SteBp) in EAN films confined between parallel polar glass plates, with gradient directions along the plates. Diffusion time was 26.65 ms, T_2 relaxation delay $\tau = 5.63$ ms, gradient duration $\delta = 1$ ms, gradient amplitude was varied in the range 0.32 - 15 T/m.



Figure S9. Diffusion coefficient of EA cation after placing EAN confined between polar glass plates in a magnetic field of 9.4 T using a standard stimulated echo pulse sequence (Ste) (black circles) and using a stimulated echo with bipolar pulsed field gradients (SteBp2) (red circles). *D* was measured along the plates. T = 293 K.



Figure S10. ¹H NMR T_2 relaxation decays for protons of **A**) –NH₃, **B**) –CH₂– and **C**) – CH₃ chemical groups of EA cations in EAN films confined between parallel glass plates at different times after placement in magnetic field of the 9.4 T of NMR spectrometer. T = 293 K.



Figure S11. Chemical structure of aprotic phosphonium bis(oxalato)borate $[P_{6,6,6,14}][BOB].$

Diffusion of EAN in the direction normal to the plates

In the general case of diffusion of fluids in a restricted geometry, three regimes of diffusion can be distinguished, which are determined by the ratio of the "pore" diameter, d, to the diffusion length, $L \approx \sqrt{(D_0 t_d)}$.² (i) In the regime of a short diffusion time, the mean squared displacements of the particles are much smaller than the pore diameter ($L \ll d$). Therefore, only particles near the pore wall have a chance to collide with the wall and the mean value of the diffusion coefficient is close to D_0 . (ii) In the regime of intermediate diffusion time, $L \sim d$, a significant fraction of the particles will collide with the pore wall. As a result of this, the apparent mean, D, is a descending function of t_d . (iii) In the long diffusion time regime, $L \gg d$, all fluid particles are equally hindered in their diffusion by the walls and their displacement is $\sim d$. The mean apparent D is thus a decreasing function of t_d (see Eq. (S1)):

$$D \sim t_d^{-1} \tag{S1}$$

Planar restriction (diffusion between parallel plates) is one of simplest regular geometries in which diffusion of a confined liquid has been analytically resolved. The expression for the DD can be presented in the following form, which exactly describes diffusion decays of molecular liquids for all regimes of diffusion in this geometry (see Eq. (S2)):³

$$A(\delta, \Delta, g) = \frac{2\left[1 - \cos(\gamma g \,\delta d)\right]}{(\gamma g \,\delta d)^2} + 4(\gamma g \,\delta d)^2$$

$$\times \sum_{n=1}^{\infty} \left\{ \frac{1 - (-1)^n \cos(\gamma g \,\delta d)}{\left[(n\pi)^2 - (\gamma g \,\delta d)^2\right]} \times \exp\left(-\frac{n^2 \pi^2 D^* \Delta}{d^2}\right) \right\}$$
(S2)

where D^* is the diffusion coefficient "undistorted" by collisions with walls. There is also a number of simulations describing diffusion of molecules for simple non-associated liquids between flat planes in their normal direction. The interaction of molecules with the plane surface is then characterized only by elastic collisions, which is in agreement with Eq. (S2).³

Scrutiny of both the form and diffusion time dependences of the experimental DDs for diffusion normal to barriers (see Figs. S5 and S6) reveals that there is a dependence of the DDs on t_d , which is typical of the intermediate diffusion time regime. *L* calculated as $L \approx \sqrt{(D_0 t_d)}$ is in the range of 1.7 - 7.5 µm and is comparable to the plate spacing, ~ 4 µm. This also corresponds to the intermediate diffusion time regime. Therefore, an iterative procedure (Eq. (S2)) was applied. The equation was solved with the number of iterations being varied up to 1000. The separation between planes was first estimated by weight and thickness as mentioned above, but then used as a fitting parameter, together with $D^* = 5.6 \cdot 10^{-11} \text{ m}^2/\text{s}$, to better match the experimental time-dependent DDs. One of the peculiarities of diffusion is that for very regular distances between planes, DDs usually demonstrate a so-called "diffusion diffraction" effect, i.e., periodic oscillations on DDs.² No such oscillations on DDs were detected in these our experiments (Figs. S5 and

S6). According to a previous study,⁴ "diffusion diffraction" effects should only occur if the distribution of distances between plates is rather narrow, which is evidently not the case in our experiment. Therefore, we tried a number of distributions of *d* such as Gaussian and log-Gaussian ones to fit the experimental DDs in Figs. S5 and S6 without identifying any satisfactory match. The best fits were obtained with an empirically chosen discrete distribution of *d* (see Fig. S12). These best fits of calculated DDs to the experimental ones are shown in Figs. S5 and S6 by solid lines and they describe the experimental DDs satisfactorily well. The mean distance between planes in these simulations is 4.1 μ m, which agrees rather well with direct measurements using two different approaches (~3.8 μ m and ~4.5 μ m).



Figure S12. EAN layer thickness (d) distribution used to fit DDs of EA for the diffusion normal to the plates (see Figs. S5 and S6).

Table S1. Diffusion coefficients of ethylammonium cations (in m^2/s) and ¹H NMR T_1 and T_2 relaxation times (in seconds) of protons of different chemical groups of ethylammonium cations at 293 K, measured for bulk EAN and for EAN confined between the glass plates.

EAN cation groups	-CH ₂ -	-CH3	$-\mathbf{NH_3}^+$
Bulk D	$(2.81 \pm 0.1) \cdot 10^{-11}$		
Confined D	$(6.92 \pm 0.1) \cdot 10^{-11} \rightarrow (2.98 \pm 0.1) \cdot 10^{-11}$		
Bulk T ₁	0.67 ± 0.01	0.88 ± 0.01	0.39 ± 0.01
Confined T ₁	$(0.79 \rightarrow 0.63)$ ± 0.01	$(0.97 \to 0.80)$ ± 0.01	$(0.49 \rightarrow 0.39)$ ± 0.01
Bulk T ₂	0.31 ± 0.01	0.51 ± 0.01	0.11 ± 0.05
Confined T ₂	$(0.050 \rightarrow 0.049) \pm 0.001$	$(0.080 \rightarrow 0.070) \pm 0.001$	$(0.005 \rightarrow 0.030) \pm 0.0005$

References

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