AC permittivity of confined water in the presence of a static field

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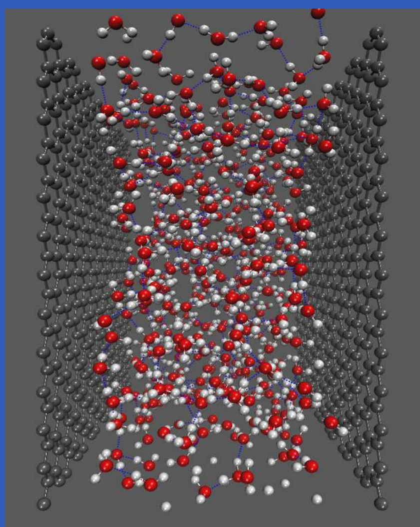
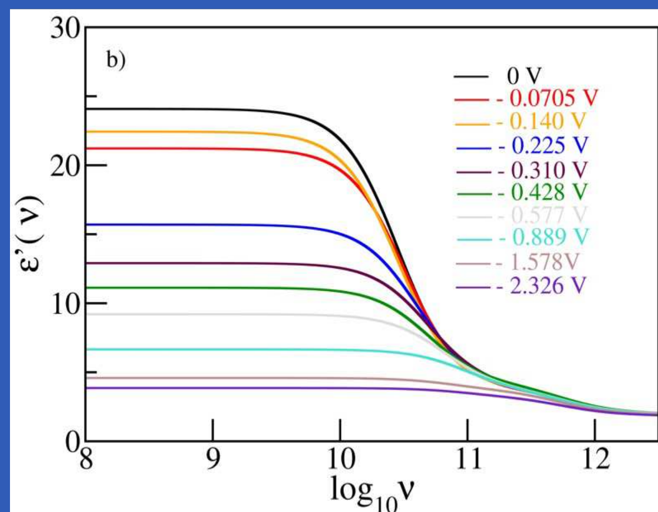
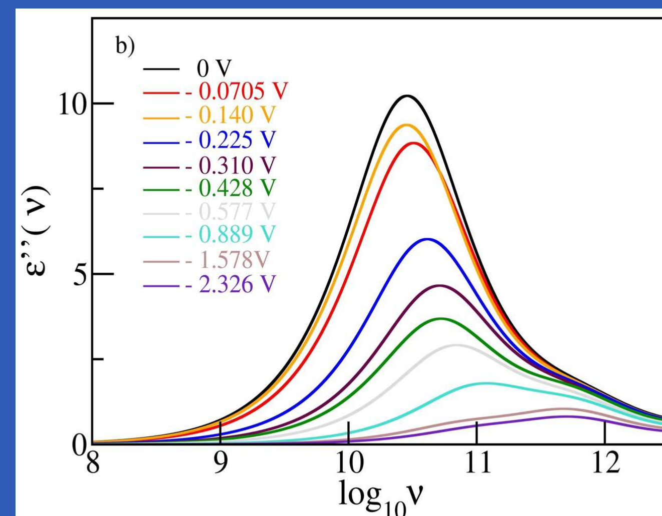






$$\varepsilon = \varepsilon' - \mathrm{i}\,\varepsilon''$$

Interfacial Phenomena & Dynamics in Electrochemical Systems,
Division of Colloid and Surface Chemistry,
ACS National Meeting, Denver, Aug 22, 2024

Nanocapacitors hold promise for energy-storage and microcircuit applications

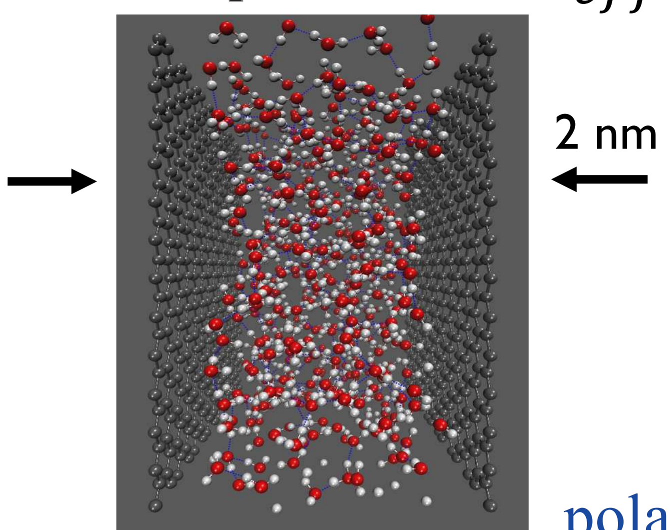
nanocapacitor arrays:

high power density, optimal recovery, cycling stability $\bar{\varepsilon}_{eff} = < \frac{1}{\bar{\varepsilon}(U)} >^{-1}$

miniaturization alleviates electric breakdown concerns

Experiments at $\boldsymbol{d = O(10^2)}$nm: ≥ 5 fold *increase of* breakdown field to $E_{max} \geq 1\mathrm{MVcm}^{-1}$. *F*urther rise expected in $O(1)$ nm slit*

Capacitance $C = \varepsilon_{eff}\varepsilon_o \frac{A}{h}$; *in linear response regime* $E \sim C\frac{U^2}{2}$



nonlinear response at elevated field, qualitative changes of dielectric behavior in ***hydration layers.*** Molecular level understanding through **all-atom modeling**

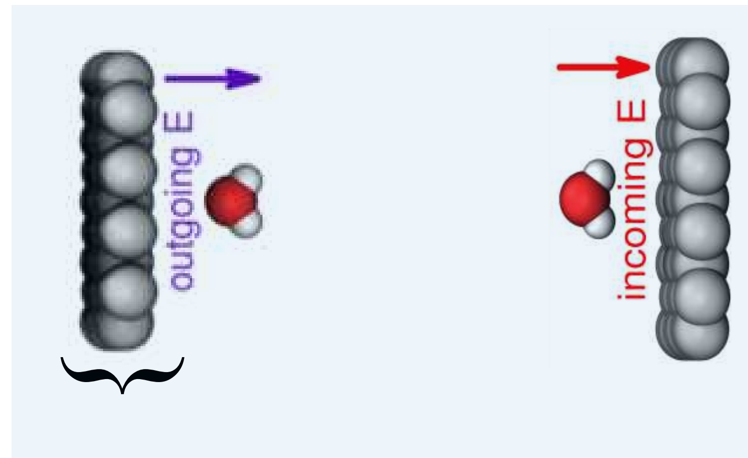
Molecular Dynamics

polarization in nanoconfined electrolyte: **dominated by the solvent**

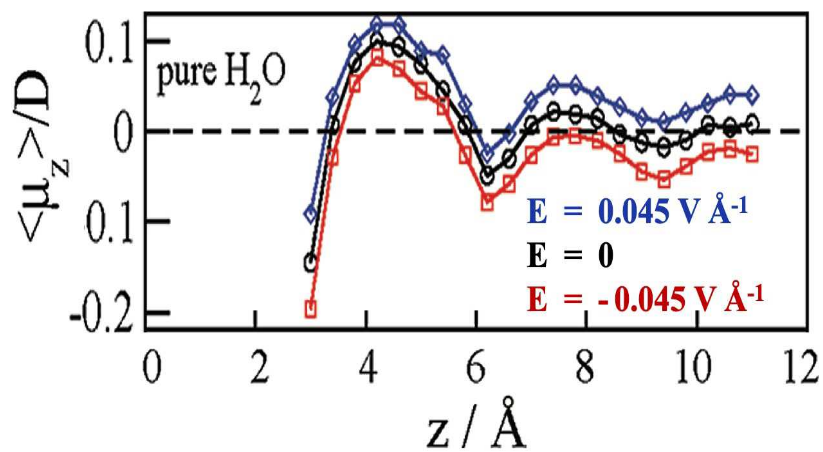
*C. R. Song, P. S. Wang, *Rev. Sci. Instrum*. **81**, 054702 (2010)

Tensorial permittivity of interfacial water (or other polar liquids)**:**
nonuniform and highly anisotropic - weaker polarization response to perpendicular field

This work concerns a less known feature: **effect of background field on *AC* responses**

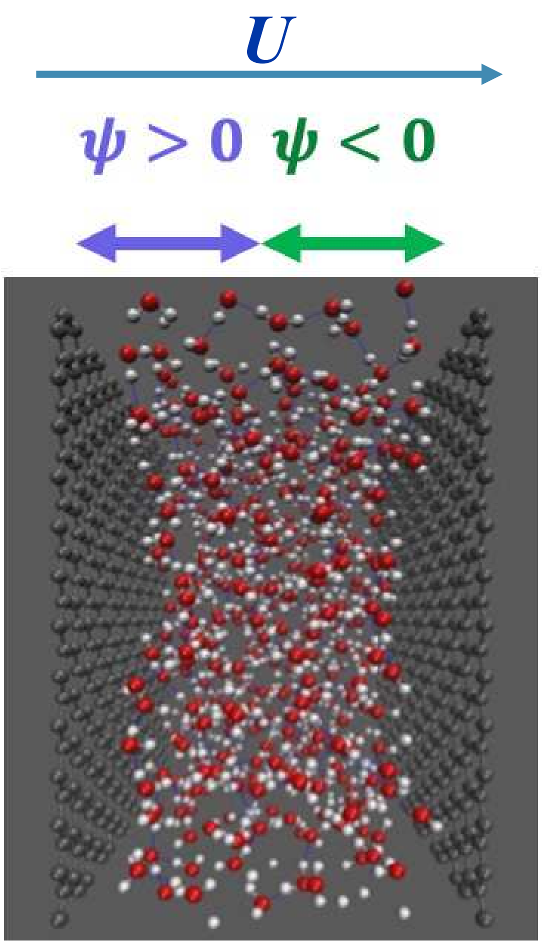


The **sign** of the field matters as induced polarization interferes with ***short-ranged*** orientation bias of asymmetric water molecules

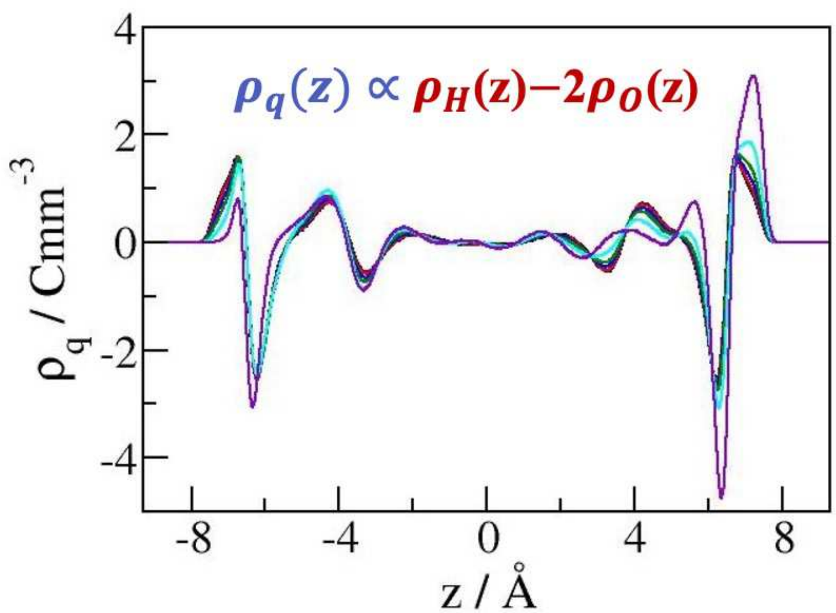


Important for *nanosized* systems: **nanocapacitors,** ion channels, membrane hydration…

Daub, Bratko, Luzar *J. Phys. Chem. C* **115,** 22393 (2011)



Charge density profiles for different voltages *U* between insulated plates ranging from *U*=0 (black) to 2.3 V (magenta)



model system: SPC/E water between graphene sheets

N. Mulpuri, D. Bratko, *J. Chem. Phys.* **158,** 134716 (2023)

$$m(z) = -\int_{-\infty}^{z} \rho_q(z')dz'$$

$$M_{ab} = L_x L_y \int_{z_a}^{z_b} m(z')dz'$$

$$M = L_x L_y \int_{-\infty}^{\infty} m(z')dz'$$

DC: Interval averaging: inverse dielectric ***difference*** constant.

$$\frac{1}{\bar{\varepsilon}_{eff}} = < \frac{1}{\bar{\varepsilon}(z)} >_{ab} = \frac{E(z)}{E_o} = \frac{1}{z_b - z_a}\int_{z_a}^{z_b} \frac{1}{\varepsilon(z)} dz = 1 - \frac{<\Delta M_{ab}>}{V_{ab} E_o \varepsilon_o}$$

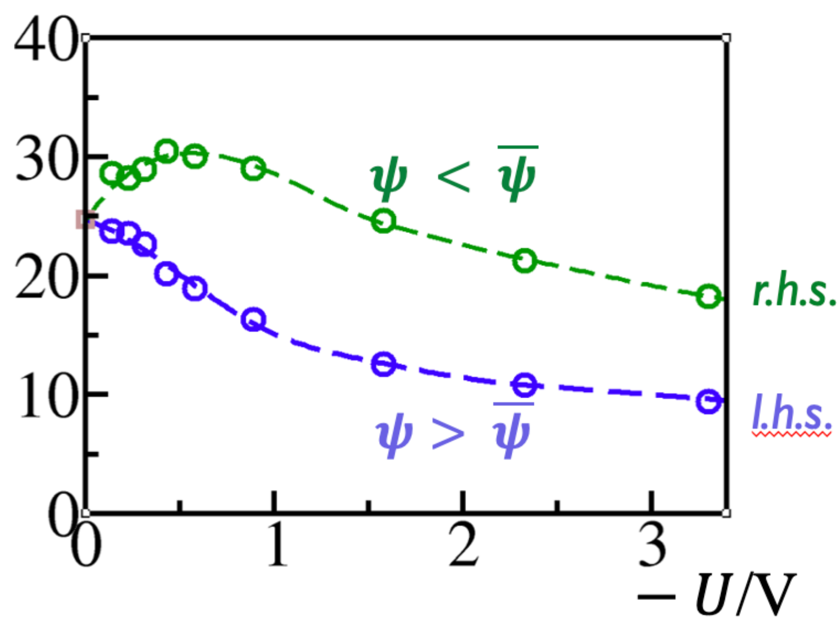
$$U_{C-C} = \psi_{right} - \psi_{left} = d\, E_o < \frac{1}{\varepsilon(z)} >_{d_{C\text{-}C}}$$

Interval–averaged ***differential*** dielectric constant from dipole fluctuations in a single layer system (no periodicity in z direction):

$$\frac{1}{\varepsilon_{d,eff}} = < \frac{1}{\varepsilon_d(z)} >_{ab} = 1 - \frac{\beta}{V_{ab}\varepsilon_o} [<M_{ab}M> - <M_{ab}><M>]$$

$$\bar{\varepsilon}_{eff} = < \frac{1}{\bar{\varepsilon}(U)} >^{-1}$$

in two half-speces



N. Mulpuri, D. Bratko, *J. Chem. Phys.* **158,** 134716 (2023)

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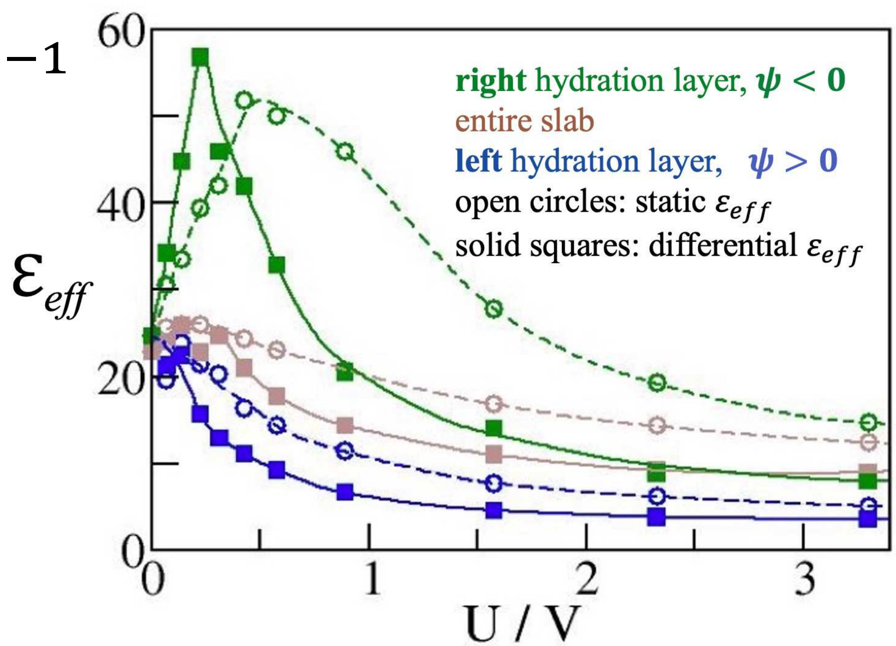


N. Mulpuri, D. Bratko, *J. Chem. Phys.* **158,** 134716 (2023)

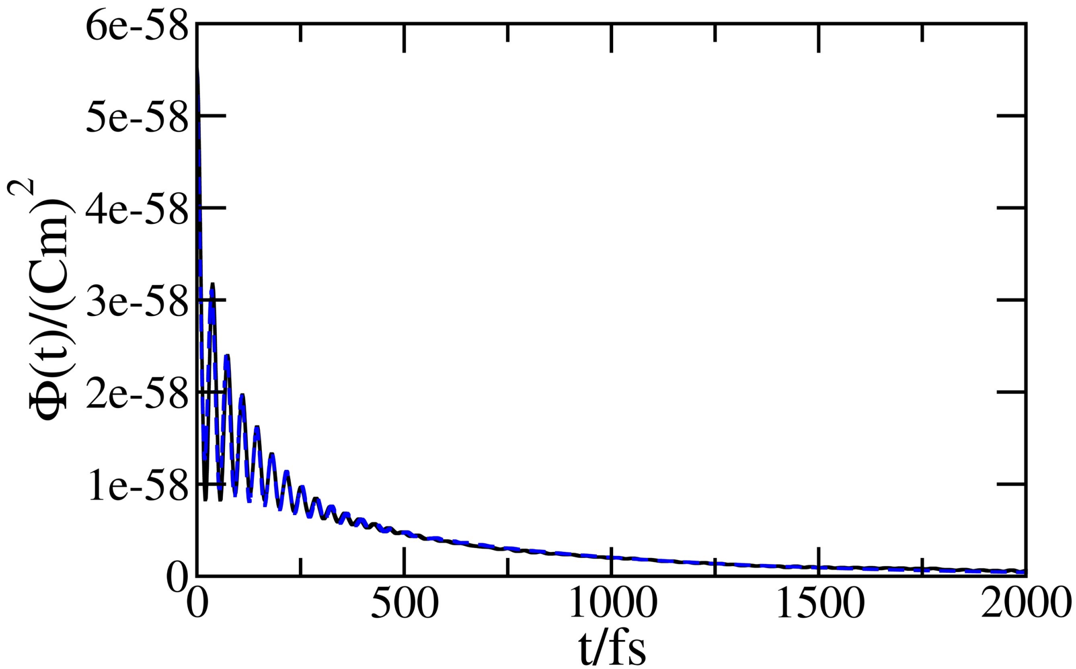
AC: frequency-dependent permittivity

$$\frac{\epsilon_\perp(f) - 1}{\epsilon_\perp(f)} = \frac{L_{if}(-\dot{\Phi}_\perp)}{\epsilon_0 k_B T V}$$

Gekle, Netz, *J.Chem. Phys.* **137**, 104704 (2012)

$$\Phi_{ab}(t) = < M_{ab}(0)M(t) > - < M_{ab} >< M >$$

Accurate calculation of $\Phi_{ab}(t)$ represents the central computational challenge

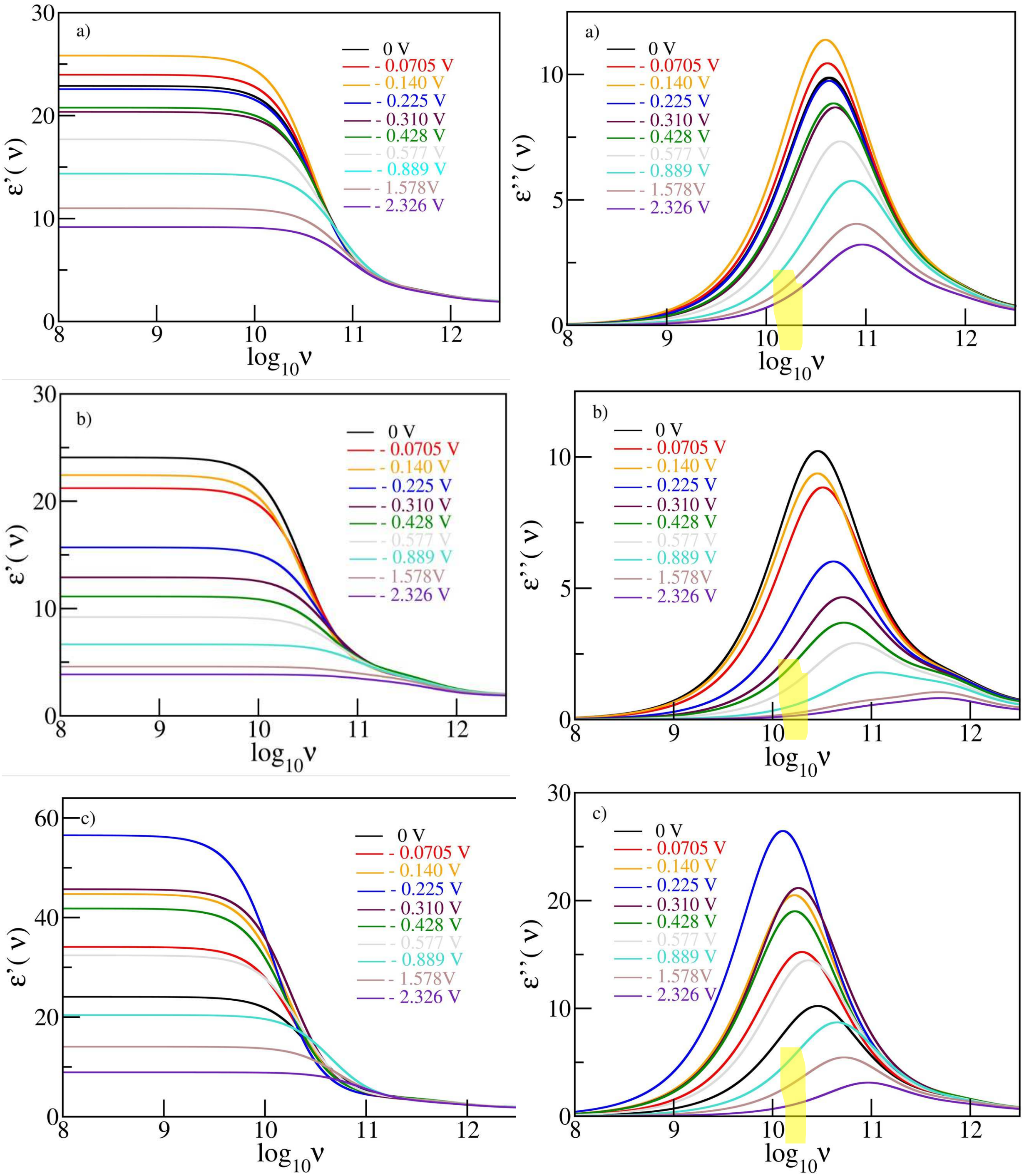


$$\varepsilon = \varepsilon' - \mathrm{i}\,\varepsilon''$$

entire pore

l.h.s. (+) plate

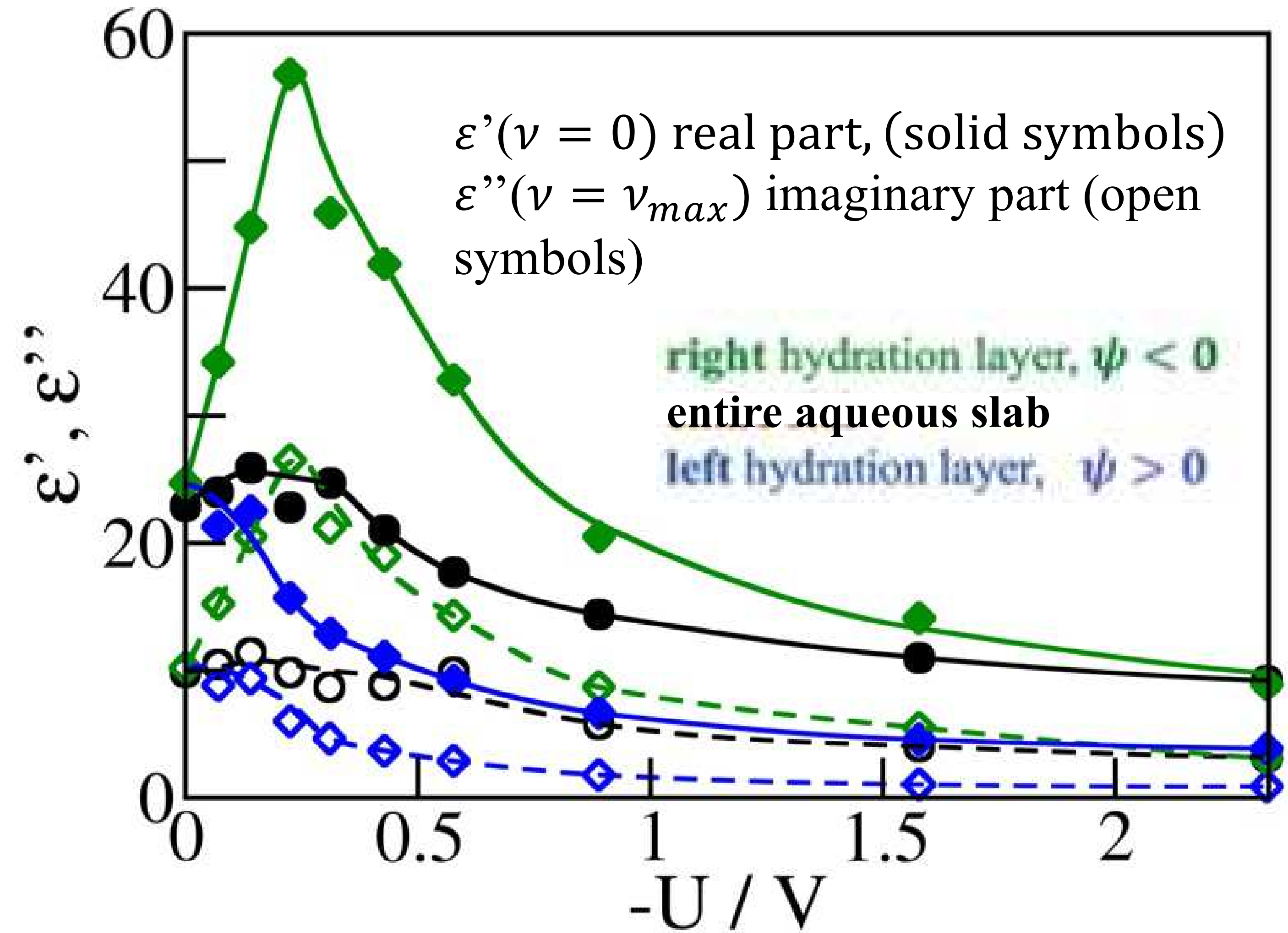
r.h.s. (-) plate



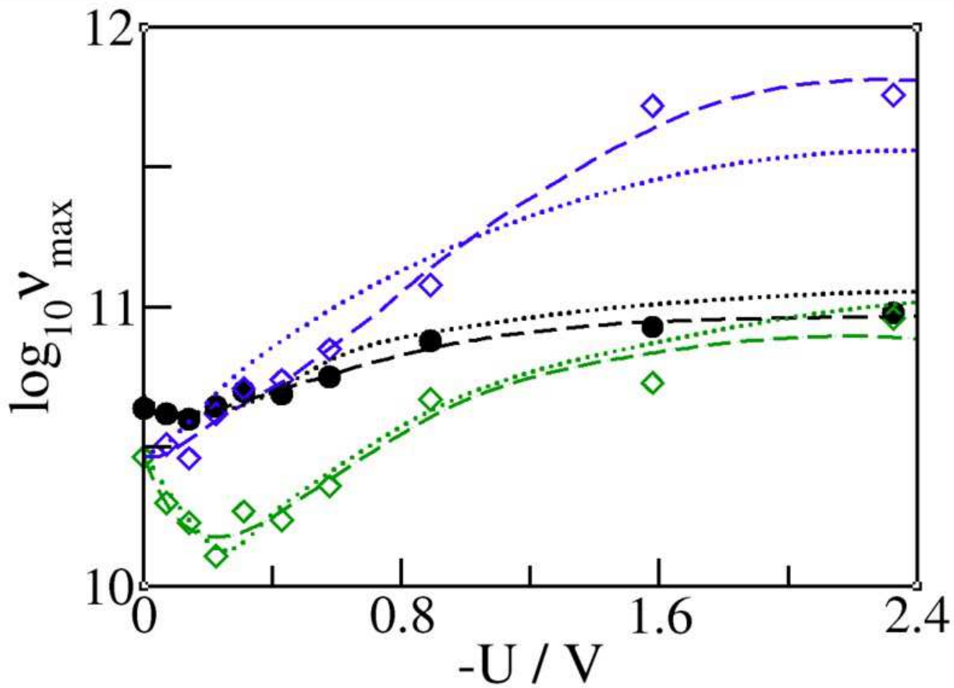
$\nu = \nu_{max}$ in bulk water

ε': real component

ε'': imaginary permittivity component



Valuable for the development of compact pulsed power systems, *e.g.* in cancer treatment, where water is the principal dielectric medium: Minatami, Y. et al. *IEEE Trans. Diel. Electronic. Diel. Insul.* **14** ,894 (2007)



$$\nu_{max} = \frac{1}{\epsilon'_{\perp}(\nu = 0)} \frac{1}{2\pi\tau_{\perp}}$$

$$\tau_{\perp} = \int_0^{\infty} \Phi_{\perp}(t)/\Phi_{\perp}(0)dt$$

Gekle, Netz, J.Chem. Phys. **137**, 104704 (2012)

5-20 fold change in ν_{max} can single out the targeted region in compact-pulsed-power therapy *etc*:
Minatami, Y. et al. *IEEE Trans. Diel. Electronic. Diel. Insul.* **14** 894 (2007)

Microwave power: $P = 2\pi\nu\varepsilon_o\varepsilon''(E,\nu)E^2V$

ε'' and ν_{max} in nanoporous particles permeated by water can be tuned using ionic functionalization so heating can be limited to the region where the particles are planted.

In summary

Coupling of *confinement* & *electric field effects* profoundly influences water's dielectric behavior:

Dielectric responses of confined water are *markedly nonlinear* under intense electric fields, *especially in interfacial layers*, where nonlinear field effects are *nonmonotonic* and strongly depend on the *polarity* of static (DC) field.

The real and imaginary components of AC permittivity in interfacial water show prominent and non-monotonic *spectral shifts* in the presence of concurrent DC field.

The magnitude of the shift is a predictable consequence of changes of the static pemittivity, while it is not significantly affected by rotational relaxation rates modified under the orienting field.

Thank you!