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Solvent mixing and ion partitioning effects in spontaneous charging and electrokinetic flow of liquid-liquid interface

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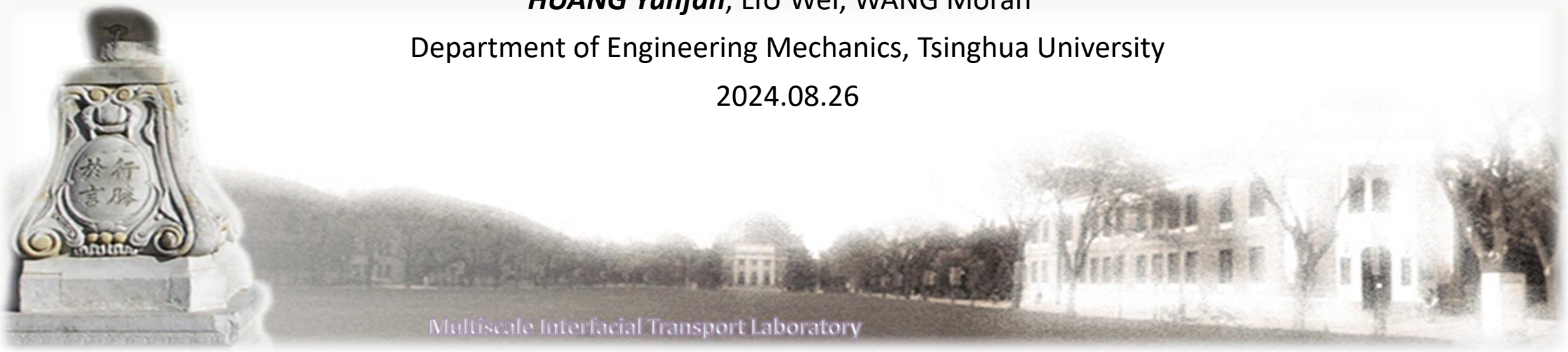
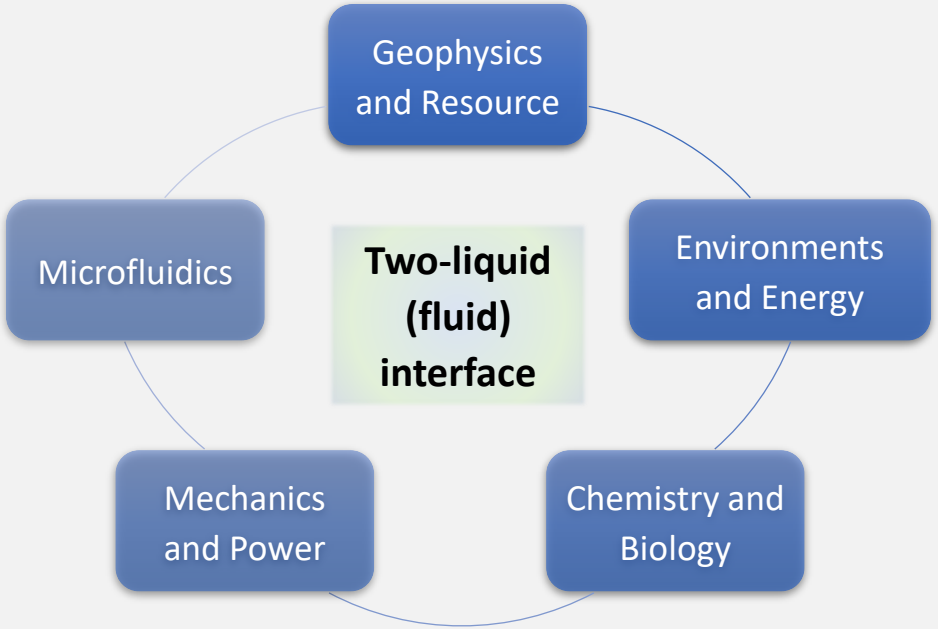
2024.08.26



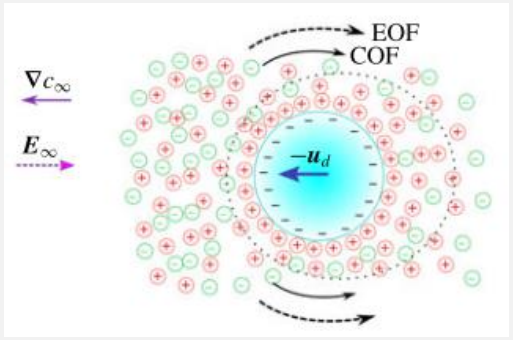
Contents

- **Background & Motivation: regulation of liquid-liquid interface dynamics**
- Methods: diffuse interface modeling with adjustable free energy profile
- Results & Discussions: solvent mixing effect and ion partition effect
- Conclusions

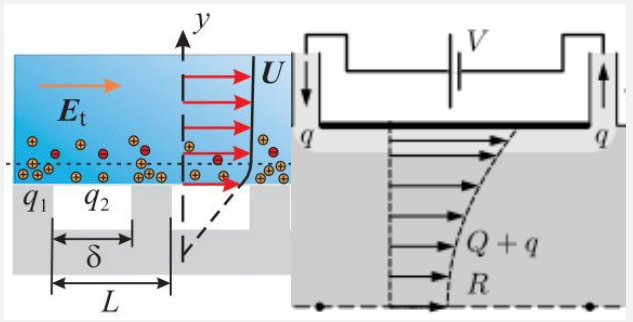
Background: Regulation of two-liquid flow and transport by electric field



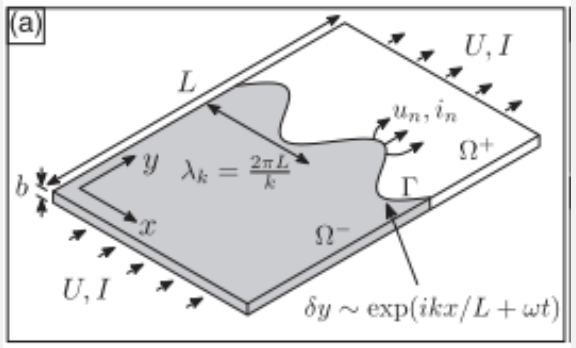
Electric field plays an essential role in various fields related to **two-liquid flow**!



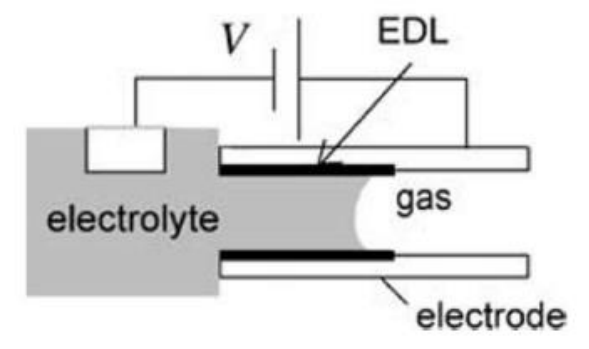
Droplet manipulation



Electrokinetic pump



Suppressing viscous fingering



Electrokinetic displacement

[1] Yang, Shin, & Stone. Diffusiophoresis of a charged drop. *Journal of Fluid Mechanics* **852**, 37-59 (2018).

[2] Belyaev & Vinogradova, Electro-osmosis on Anisotropic Superhydrophobic Surfaces. *Physical Review Letters*, **107**, 098301 (2011).

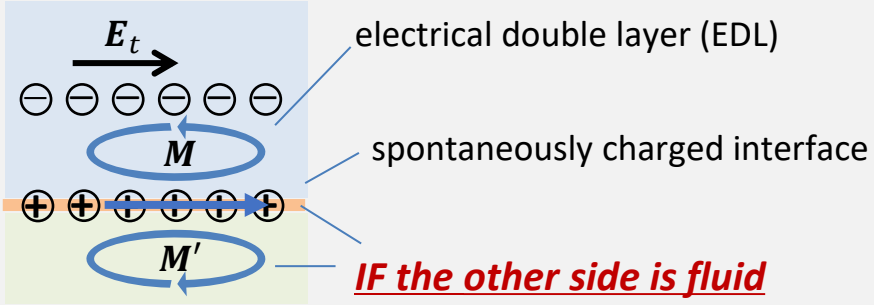
[3] Rabbani, *et al.* Suppressing viscous fingering in structured porous media. *Proceedings of the National Academy of Sciences* **115**, 4833-4838 (2018).

Motivation 1: Interfacial structure in two-liquid electrokinetics

Electrolyte solution: Conductive dielectrics

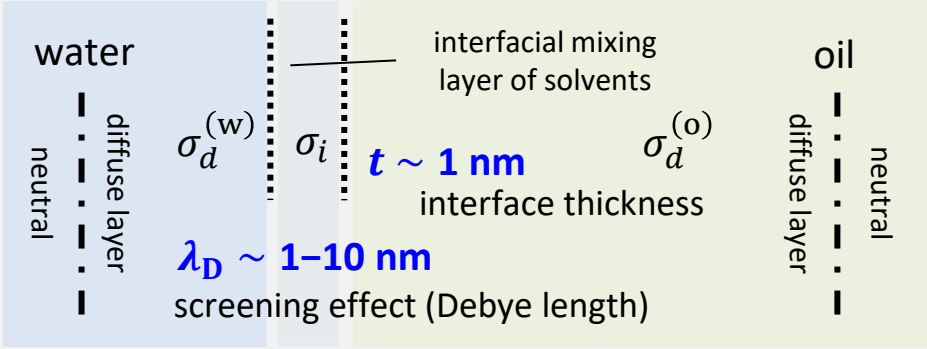
*Electro-**kinetics***: co-transport of ions & fluid inside EDL

- **Phys-chem** effect → Spontaneous charging
- Torque by $\boldsymbol{E}_t$ → Shear **flow of charged fluid**



Two-liquid v.s. Solid-liquid interface?

- ✓ *Continuous transition* of solvent properties
- ✓ *Interfacial partition* and adsorption of ions
- ☐ Interface deformation and ***shear-driven flow***
- ☐ Interphase charge transport and polarization

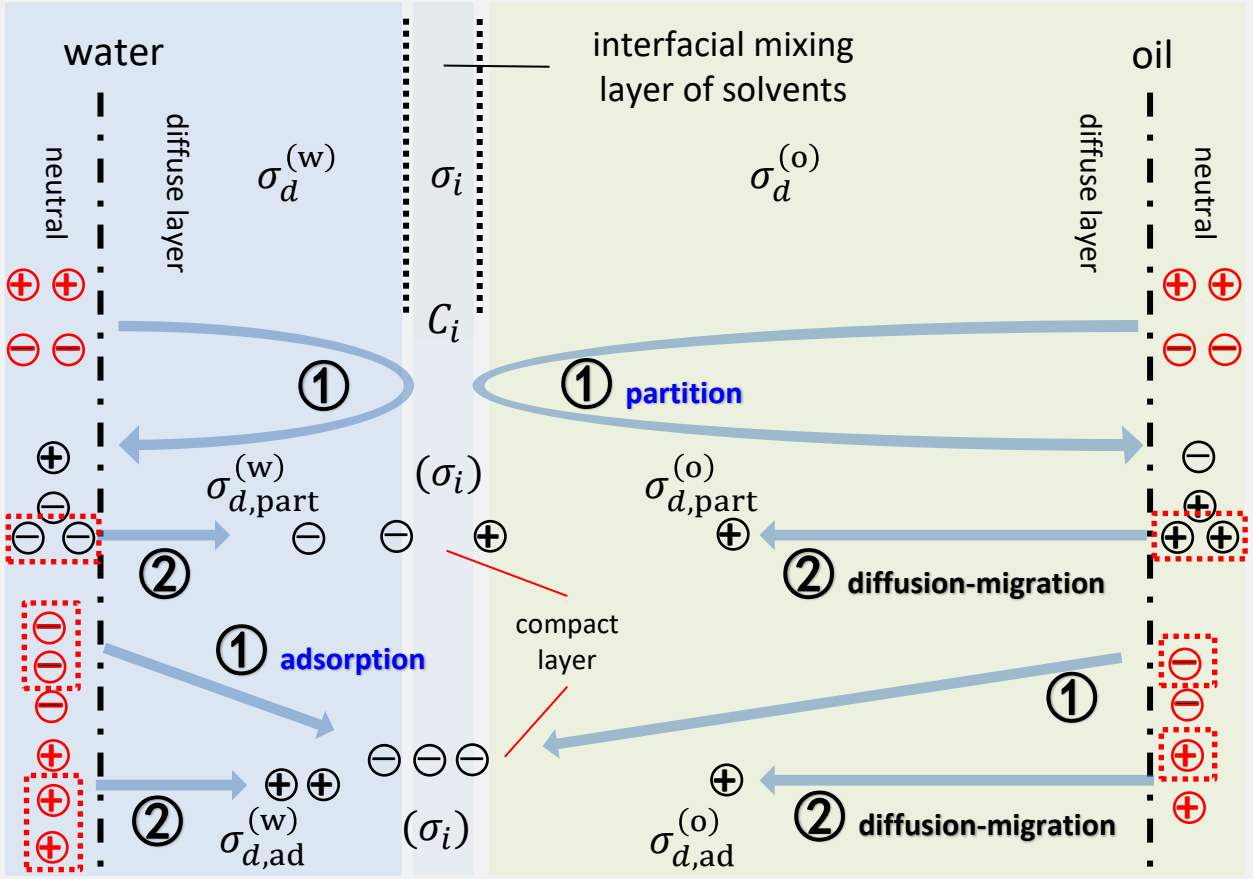


Motivation 1: Accurate resolution of interface?

- Potential drop within **finite-thickness** solvent mixing layer
- Interfacial stress-matching condition under **large shear stress**

Bazant. Electrokinetics meets electrohydrodynamics. *Journal of Fluid Mechanics* **782**, 1-4 (2015).

Motivation 2: Interfacial charging mechanisms of two-liquid interface



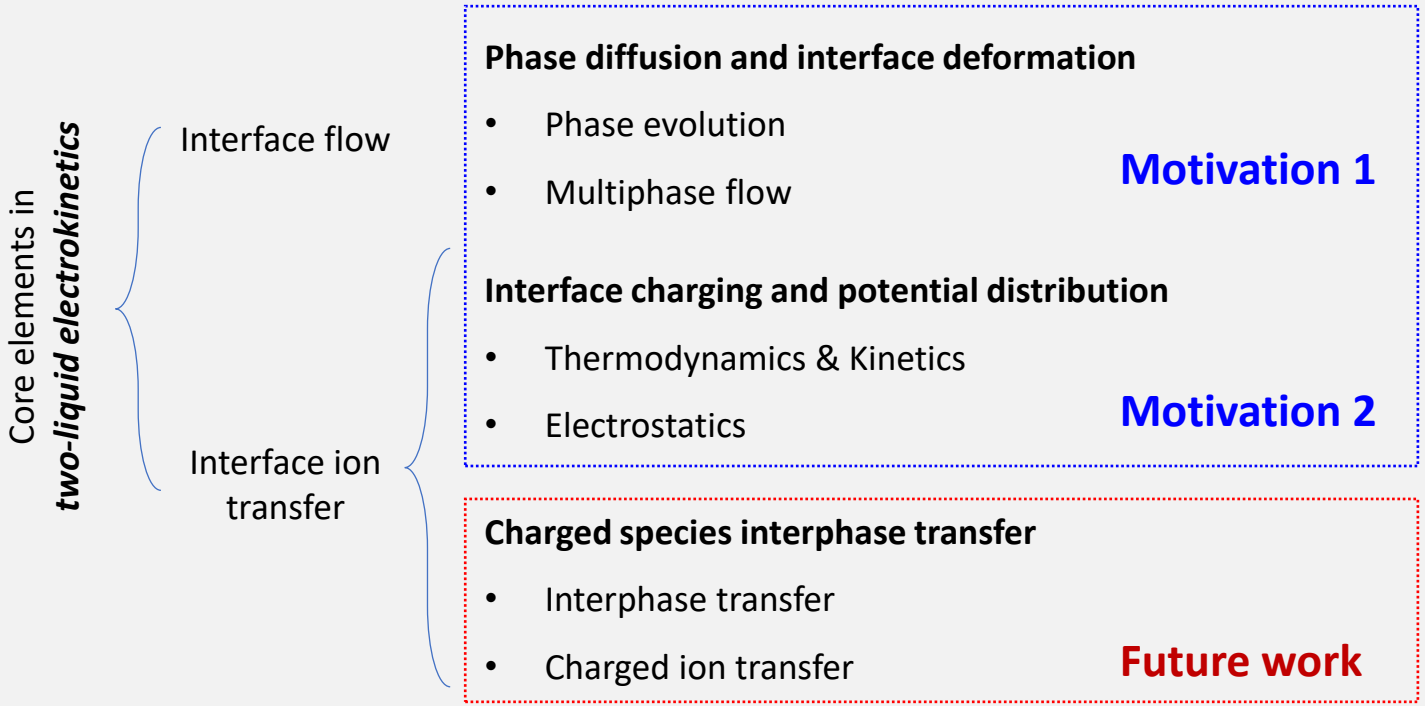
- ***Partition***: ***between two bulk phases***
  - ✓ **Charging mechanism I:** ***imbalance*** *partitioning*
  - ✓ **Description:** partition coefficient
- ***Adsorption***: ***between surface & bulk phases***
  - ✓ **Charging mechanism II:** ***specific*** *adsorption*
  - ✓ **Description** : surface complexation
- ◆ **Comparison: what about solid-liquid interface?**
  - ■ almost depletion inside, single diffuse layer
  - ■ only adsorption-induced, fixed adsorption site

Motivation 2: Mechanism-based unified description?

- Effect of **solute permittivity** on ion partition behavior
- Effect of **solution property** on ion adsorption behavior

Volkov, Deamer, Tanelian, & Markin. Electrical double layers at the oil/water interface. *Progress in Surface Science* **53**, 1-134 (1996).

Literature review and our focus



- **Lack of studies → Challenges**
  - ☐ interface deformation
  - ☐ multiphysics & multiscale
  - ☐ non-linear transport
  - ☐ quantitative comparison
- **Technical issues → Solutions**
  - ☐ sharp/diffuse interface?
  - ☐ charging mechanisms?
  - ☐ electrical field strength?
  - ☐ verification & validation?

In this work, we will address the following perspectives in ***two-liquid interface electrokinetics***, which have not been well understood

- **Motivation 1: diffuse feature**, i.e., **solvent mixing effects** (permittivity- and viscosity-related)
- **Motivation 2: charging mechanism**, i.e., **ion partition effects** (permittivity- and component-dependent)

We will choose ***two-liquid parallel electroosmosis under weak E field*** as model system, providing a promising framework for future.

[1] Ding, Jian, & Tan. Electrokinetic energy conversion of two-layer fluids through nanofluidic channels. *Journal of Fluid Mechanics* **863**, 1062-1090 (2019).

[2] Choi, Sharma, Qian, Lim, & Joo. On steady two-fluid electroosmotic flow with full interfacial electrostatics. *Journal of Colloid and Interface Science* **357**, 521-526 (2011).

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Modeling method: Diffuse interface models with modified free energy profile

Motivation 1: Accurate resolution of interface?

- ***Technical issues***: sharp/diffuse interface with interface deformation

Diffuse interface model (phase field)

- *Phase/Flow*
  - Cahn-Hilliard-Navier-Stokes equations
  - conservative form of phase field evolution
  - continuous surface and electrical forces ($\boldsymbol{F}_{\mathrm{st}}$, $\boldsymbol{F}_{\mathrm{E}}$)

$$\mu_\phi = \gamma \frac{3\varepsilon_{\mathrm{pf}}}{2\sqrt{2}}\left[-\nabla^2\phi + \frac{(\phi^2-1)\phi}{\varepsilon_{\mathrm{pf}}^2}\right], M = \chi\varepsilon_{\mathrm{pf}}^2$$

$$\boldsymbol{F}_{\mathrm{st}} = -\phi\nabla\mu_\phi,\ \boldsymbol{F}_{\mathrm{E}} = \rho_e\boldsymbol{E} - \frac{1}{2}E^2\nabla\varepsilon$$

$$\frac{\partial\phi}{\partial t} + \boldsymbol{u}\cdot\nabla\phi = \nabla\cdot M\nabla\mu_\phi\ ,\ \nabla_n\mu_\phi = 0, \nabla_n\phi = |\nabla\phi|\cos\theta$$

$$\phi^{\mathrm{eq}} = \tanh\left(\frac{D_{\mathrm{wi}}}{\sqrt{2}\varepsilon_{\mathrm{pf}}}\right)$$

Thickness of phase interface $\propto \sqrt{2}\varepsilon_{\mathrm{pf}}$

$$\rho\frac{\partial\boldsymbol{u}}{\partial t} + \rho\boldsymbol{u}\cdot\nabla\boldsymbol{u} = -\nabla p + \nabla\cdot\mu\nabla\boldsymbol{u} + \boldsymbol{F}_{\mathrm{st}} + \boldsymbol{F}_{\mathrm{E}}$$

Better physical foundation of scale parameters

Anderson, McFadden, & Wheeler. Diffuse-interface methods in fluid mechanics. *Annual Review of Fluid Mechanics* **30**, 139-165 (1998).

Modeling method: Diffuse interface models with modified free energy profile

Motivation 2: Mechanism-based unified description?

- ***Technical issues***: multiphysics & multiscale charging mechanisms

Modified free energy model

- *Charge/Potential*
  - modified Poisson-Boltzmann (Nernst-Planck) equation
  - phase-parameter-dependent free energy profile $\Delta G(\phi)$
  - phys-chem property-dependent $\Delta G^{(i)}$ partition/adsorption

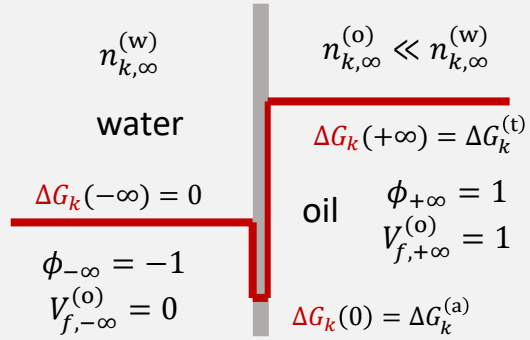
$$\nabla \cdot \left(\nabla n_k + n_k \nabla \frac{z_k e\varphi + \Delta G_k(\phi)}{k_{\mathrm{B}} T} \right) = 0$$

$$\nabla \cdot (\varepsilon \nabla \varphi) = -\rho_e + \rho_{\mathrm{fix}}, \rho_e = \Sigma_k z_k e n_k$$

Partition: $\Delta\varphi_\infty \equiv -\frac{\Delta G_+^{(\mathrm{t})} - \Delta G_-^{(\mathrm{t})}}{2e}$

Adsorption: $\rho_{\mathrm{fix}} = \sigma_{ll}/d_{\mathrm{ad}}$ OR

$$\sigma_s = 2d_{ad} \exp\left(-\frac{\Delta G_s^{(\mathrm{a})}}{k_{\mathrm{B}} T}\right) \rho_s$$



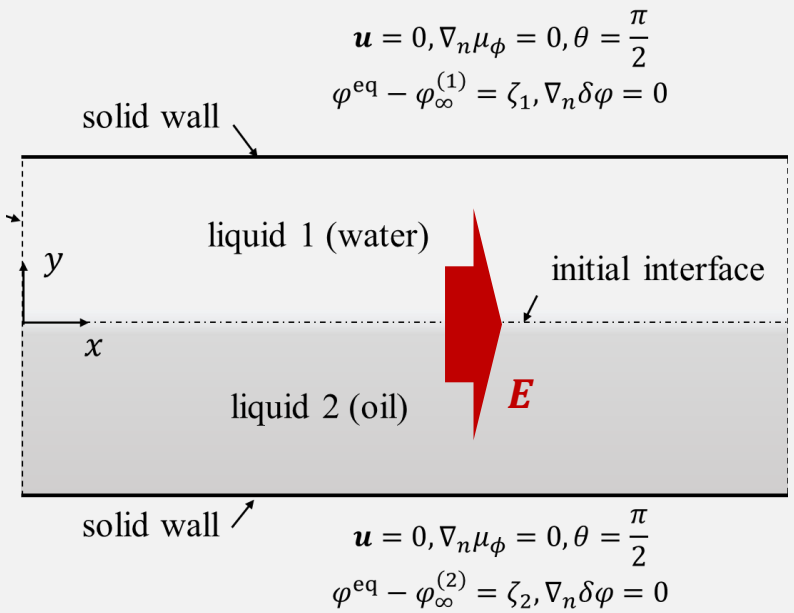
Potential to incorporate multi-physico-chemical effects

[1] Krishna & Wesselingh. The Maxwell-Stefan approach to mass transfer. *Chemical Engineering Science* **52**, 861-911 (1997).

[2] Leroy, Jougnot, Revil, Lassin, & Azaroual. A double layer model of the gas bubble/water interface. *Journal of Colloid and Interface Science* **388**, 243-256 (2012).

Simulation method: Physical assumptions and system/solver setup

- **Physical assumptions**
  - **Constant & uniform property, small surface charge**
    - Constant bulk/surface property
    - $n_\infty^{(\mathrm{w})} = 1\ \mathrm{mM},\ \varepsilon^{(\mathrm{w})} = 80,\ \lambda_\mathrm{D}^{(\mathrm{w})} \simeq 10\ \mathrm{nm}$
  - **Weak external electric field as perturbation**
    - Quasi-equilibrium perturbation
    - $\varphi = \tilde{\varphi}^{eq} + \delta\varphi, n_i = \tilde{n}_i^{eq} + \delta n_i, E_\mathrm{ext} \ll E_\mathrm{surf}$



- **System/Solver setup**
  - **Material property**: linear interpolation $(\varepsilon, \mu, \rho)(\phi) = \sum_i (\varepsilon, \mu, \rho)^{(i)} V_\mathrm{f}^{(i)}$
    - $\varepsilon_\mathrm{pf} = 0.5\ \mathrm{nm},\ d_\mathrm{ad} = \sqrt{2}\ \mathrm{nm},\ \chi = 10\ \mathrm{m \cdot s/kg}$ → balance accuracy (↓) & cost (↑)
  - **Numerical method**: finite element method
    - $\Delta_\mathrm{max}^\mathrm{bulk} = 2.5\ \mathrm{nm}, \Delta_\mathrm{max}^\mathrm{surf}/\varepsilon_\mathrm{pf} = 0.1$; ϕ 2nd | φ 2nd | $(\boldsymbol{u}, p)$ 2nd+ 1st → suppress spurious force & velocity

[1] Masliyah & Bhattacharjee. *Electrokinetic and Colloid Transport Phenomena*. (John Wiley & Sons, Inc., 2006).

[2] Saville. ELECTROHYDRODYNAMICS: The Taylor-Melcher Leaky Dielectric Model. *Annual Review of Fluid Mechanics* **29**, 27-64 (1997).

[3] Sweeney, Scriven, & Davis. Gradient theory of the electric double layer at hydrocarbon–water interfaces. *The Journal of Chemical Physics* **87**, 6120-6127 (1987)

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Verification: proposed diffuse v.s. sharp interface model for $(\varepsilon, \mu)_o = (\varepsilon, \mu)_w$

System

default setups

- $W = 2d = 1\ \mu\text{m}, \gamma = 0.07\ \text{N/m},$
- Streamwise symmetry, periodicity
- Solid wall positively charged, i.e., $\sigma_{sl,1/2} \geq 0$
- Matched material property, i.e. $\rho_r = n_r = 1$
- $\sigma_{sl,1|2} = 0\ |\ 2\ \text{mC/m}^2, \Delta_1^2\varphi_\infty = 0\ |\ -\zeta_T$

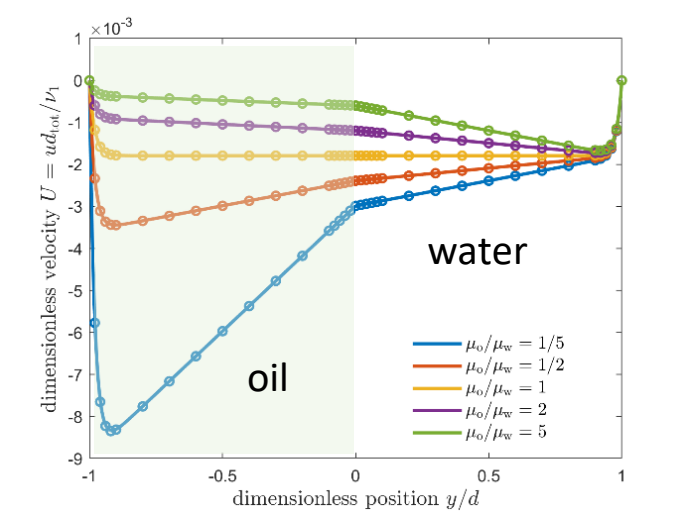
Core assumptions

sharp interface model

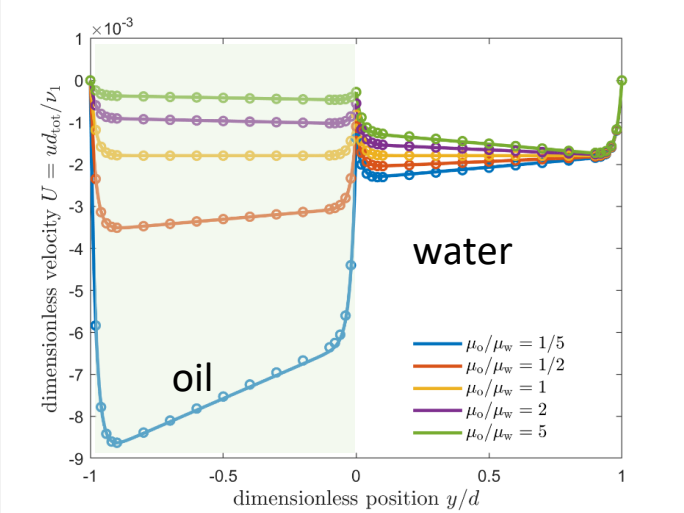
$$(\varphi_1 - \varphi_2)|_{y=0} = -\Delta_1^2\varphi_i$$

$$\left(\varepsilon_1 \frac{\partial \varphi_1}{\partial y} - \varepsilon_2 \frac{\partial \varphi_2}{\partial y}\right)|_{y=0} = -\sigma_s$$

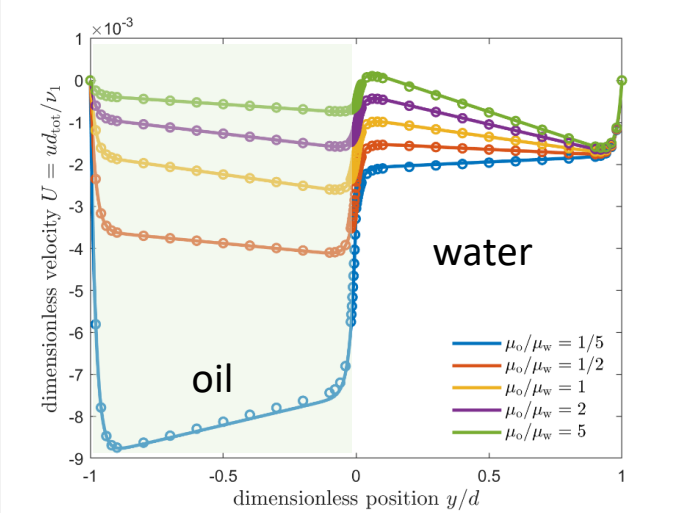
$$\left(\mu_1 \frac{\partial u_1}{\partial y} - \mu_2 \frac{\partial u_2}{\partial y}\right)|_{y=0} = -\sigma_s E$$



No interface charging



Adsorption-induced charging ($\sigma_{ll} \simeq \sigma_{sl}$)

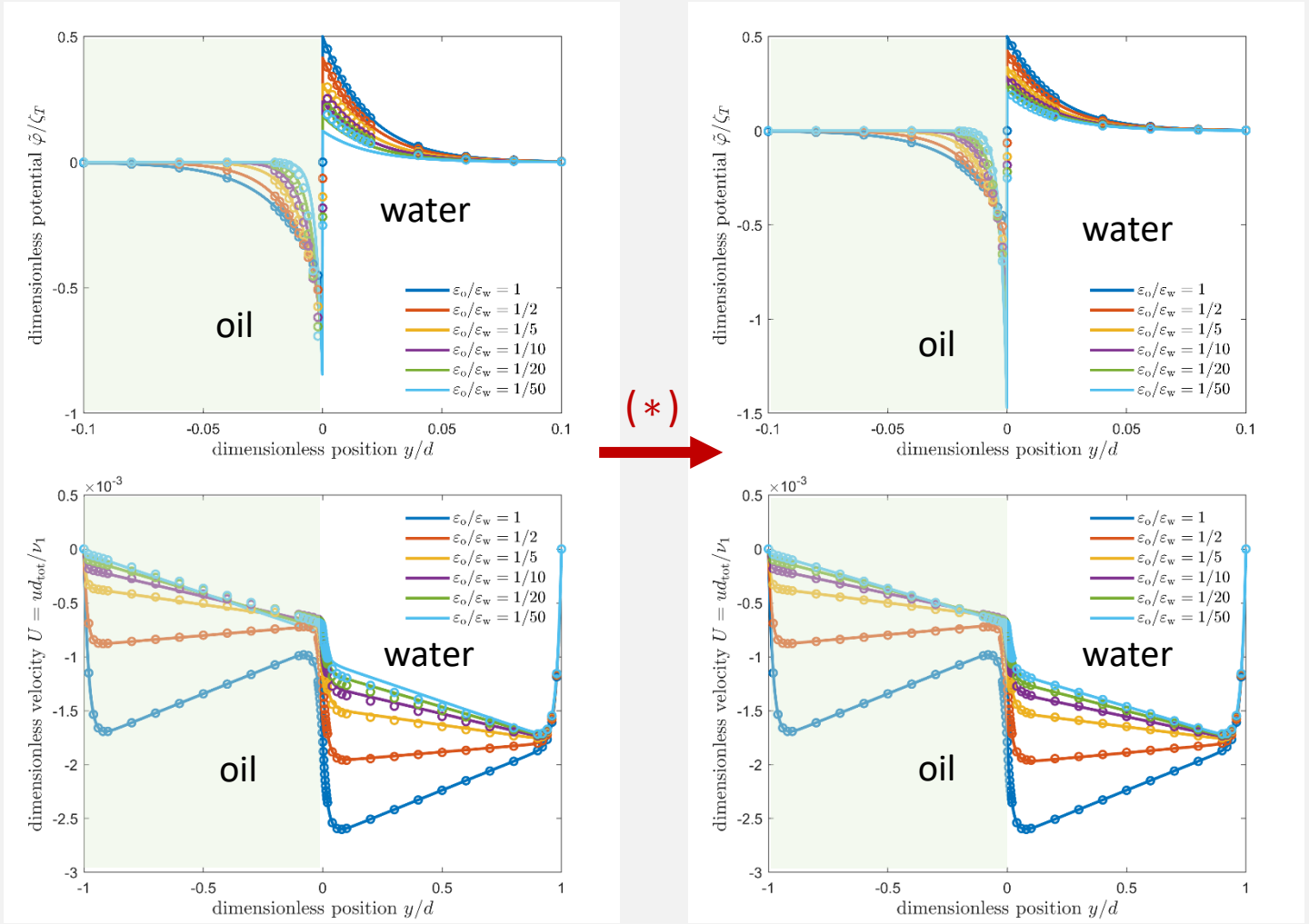


Partition-induced charging ($\Delta\varphi_\infty > 0$)

The **proposed diffuse interface agrees well** with the sharp interface model **when $\varepsilon_o = \varepsilon_w$**!

Solvent mixing effect: potential jump correction for sharp interface model

- When $\varepsilon_o \ll \varepsilon_w$, ***sharp interface model*** with $\boldsymbol{\Delta\varphi_i = 0}$ v.s. ***diffuse interface model*** as baseline



$(*)$

Partition-induced charging $\Delta\varphi_\infty > 0$, $n_o = n_w$; before (left) / after (right) correction

- Errors predicted by sharp interface model are significant (~20%), especially when $\varepsilon_o \ll \varepsilon_w$
- Semi-empirical correlation formula given through qualitive analysis & quantitative fitting

$$\delta\Delta\varphi_i = \left(\alpha_{\varepsilon,+}\partial_y\varphi_{1,0} + \alpha_{\varepsilon,-}\partial_y\varphi_{2,0}\right)\frac{\varepsilon_w - \varepsilon_o}{\varepsilon_w + \varepsilon_o}\left(1 - \frac{4|\sigma_{ll}|d_{pf}}{\varepsilon_i\zeta_T}\right) \quad (*)$$

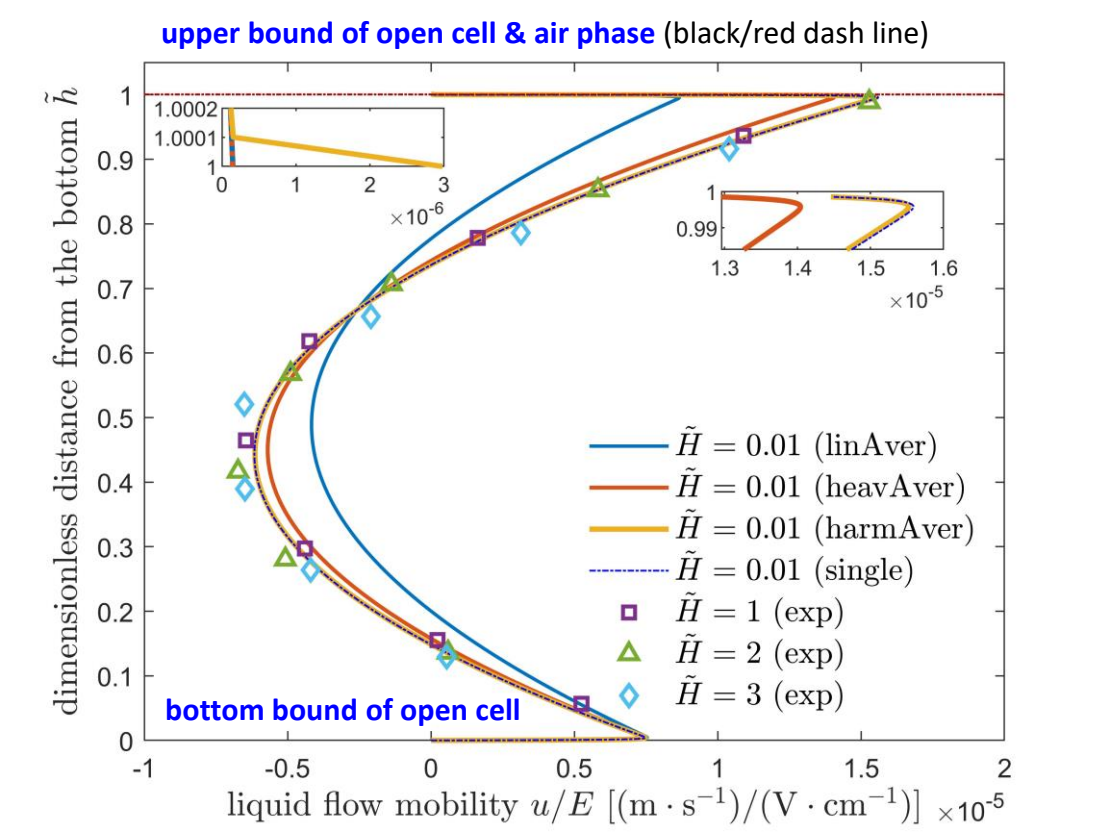
$$\alpha_{\varepsilon,\pm} = \frac{\varepsilon_i \pm \varepsilon_o}{\varepsilon_w + \varepsilon_o} \qquad \partial_y\varphi_{i,0} = (-1)^{i+1}\frac{\zeta_T}{\lambda_{D,i}}\frac{Z_i - f_i}{\sinh H_i} \qquad \varepsilon_i = \frac{\varepsilon_w + \varepsilon_o}{2}$$

- It has been verified that (details not shown):

For a **large range of n_o/n_w**, correction formula **shows great performance**!

Solvent mixing effect: viscosity interpolation strategies for $\mu_o \ll \mu_w$

- When $\mu_o \gg \mu_w$, comparisons between ***viscosity interpolation strategies*** in ***diffuse interface model***



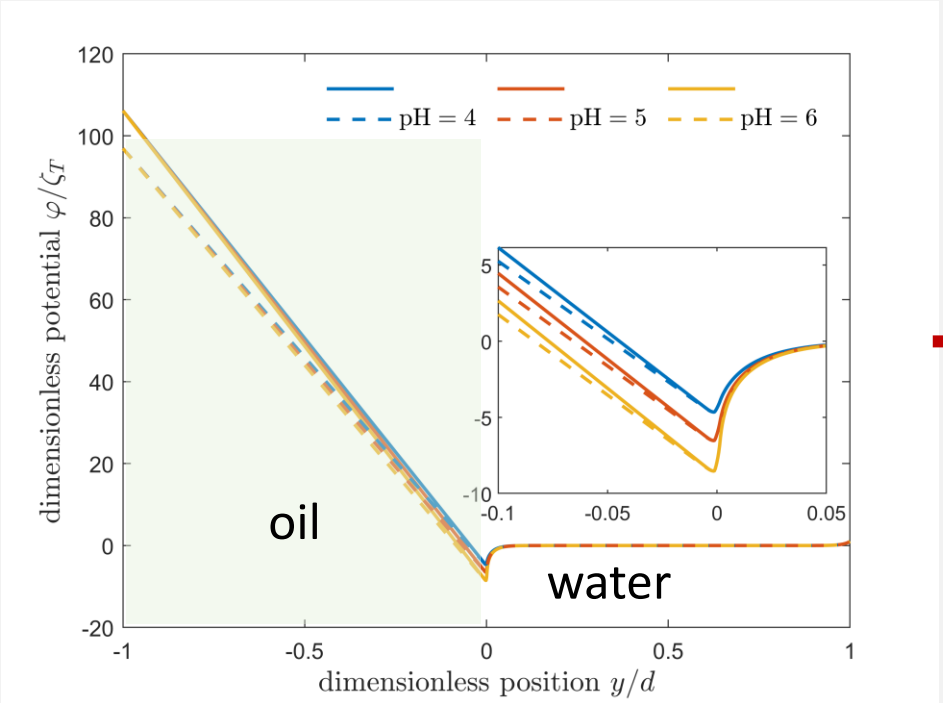
- **Plane interface measurement** of air-liquid interface charging
  - Results expressed in dimensionless distances from bottom
- **Interface properties fitted** with single phase electrokinetics
  - It is obtained that $\zeta_{\mathrm{sl}} = -110\ \mathrm{mV}$ and $\sigma_{\mathrm{lg}}^2 = -0.17\ \mathrm{C/m^2}$
- **Three interpolation strategies** of interfacial viscosity $\mu(\phi)$
  - Consistency between physical model and experiments is **strongly dependent on interpolation strategy of viscosity**.

Heaviside and harmonic interpolation strategies show the **best fitting** of the experimental results.

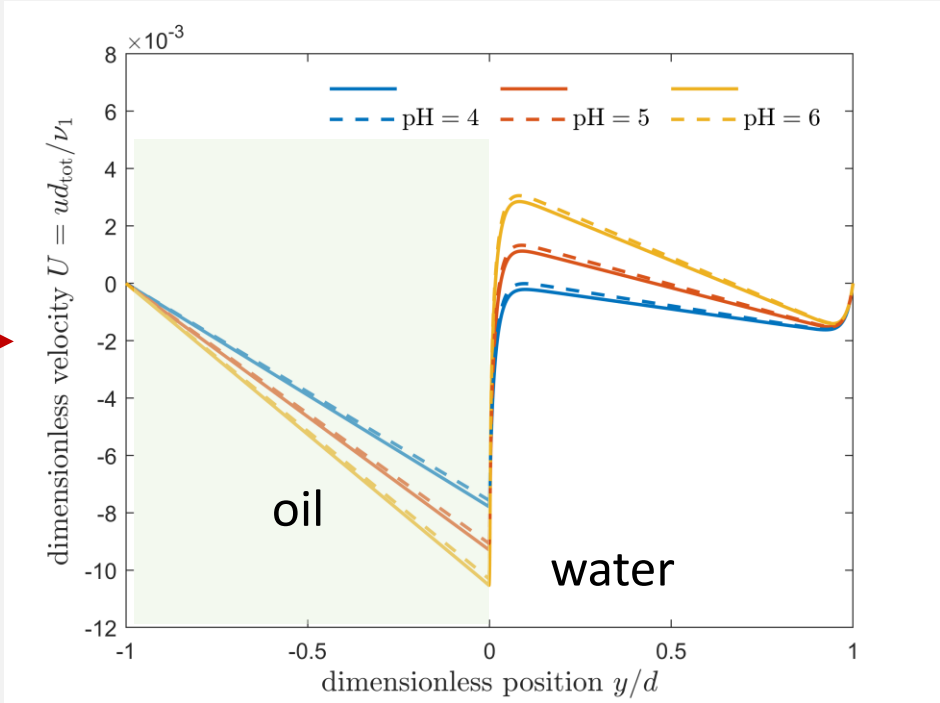
Usui, Imamura, & Sasaki. Measurement of zeta potential at aqueous solution surface by plane interface technique. *Journal of Colloid and Interface Science* **118**, 335-342 (1987).

Ion partitioning effect: monotonic dependence & adsorption dominance

- Case of non-polar oil (n-decane, **low $\varepsilon_o/\varepsilon_w \ll 1 \rightarrow n_o/n_w \ll 1$**)



Potential distribution

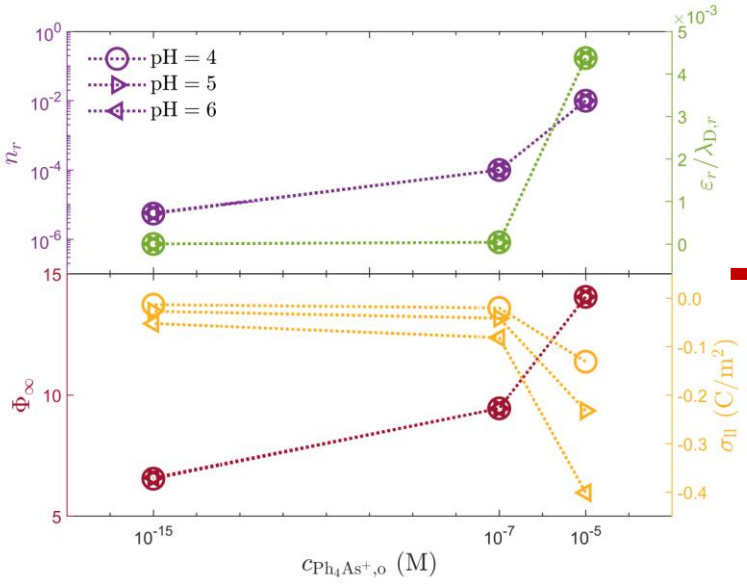


Velocity profile

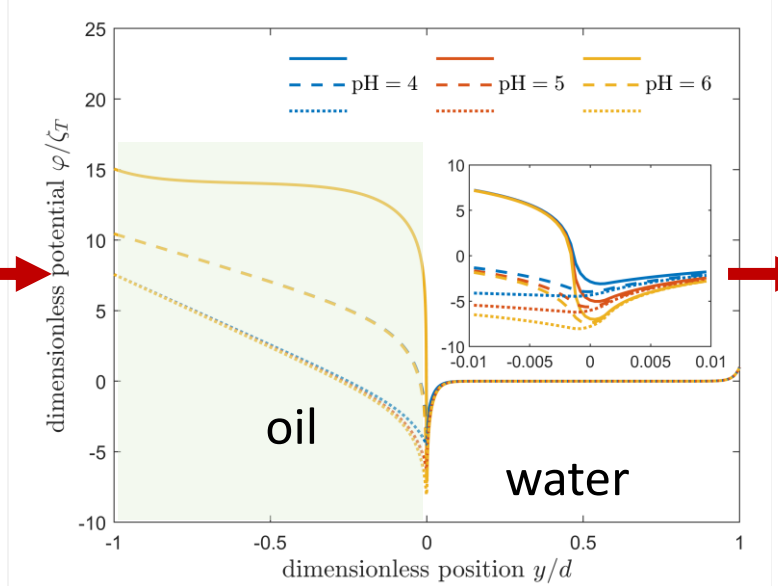
Non-polar oil with **extremely low ε_o** → **Adsorption-induced** interface charging dominates → **monotonic dependence** of potential distribution behavior; **invariant flow pattern** for different concentration and pH

Ion partitioning effect: non-monotonic dependence & mechanism competition

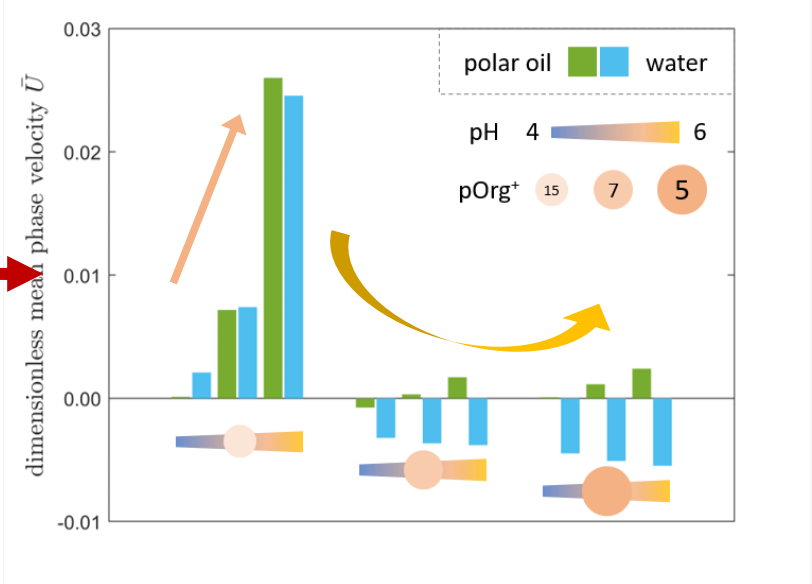
- Case of polar oil (nitrobenzene, **relatively high $\varepsilon_o/\varepsilon_w \sim 0.5 \rightarrow n_o/n_w \leq 1$**)



Interface charging parameters



Potential distribution



Mean velocity

Different impurity ion concentration and pH with **relatively high ε_o of polar oil**

→ **Competitive dominance of** interfacial charging by ion **adsorption and partition**

→ **non-monotonic dependence of velocity** on ion concentration

symmetry evolution of velocity by varying pH

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Conclusions

- In this work, we propose a **unified framework** based on the diffuse interface model and modified Boltzmann formulation to uncover the **solvent mixing effect** and **interplay of the two major charging mechanisms** in two-liquid electrokinetics. It is elucidated that the velocity profile of two-liquid flow can be regulated using electroosmosis effect through the modification of physico-chemical properties.

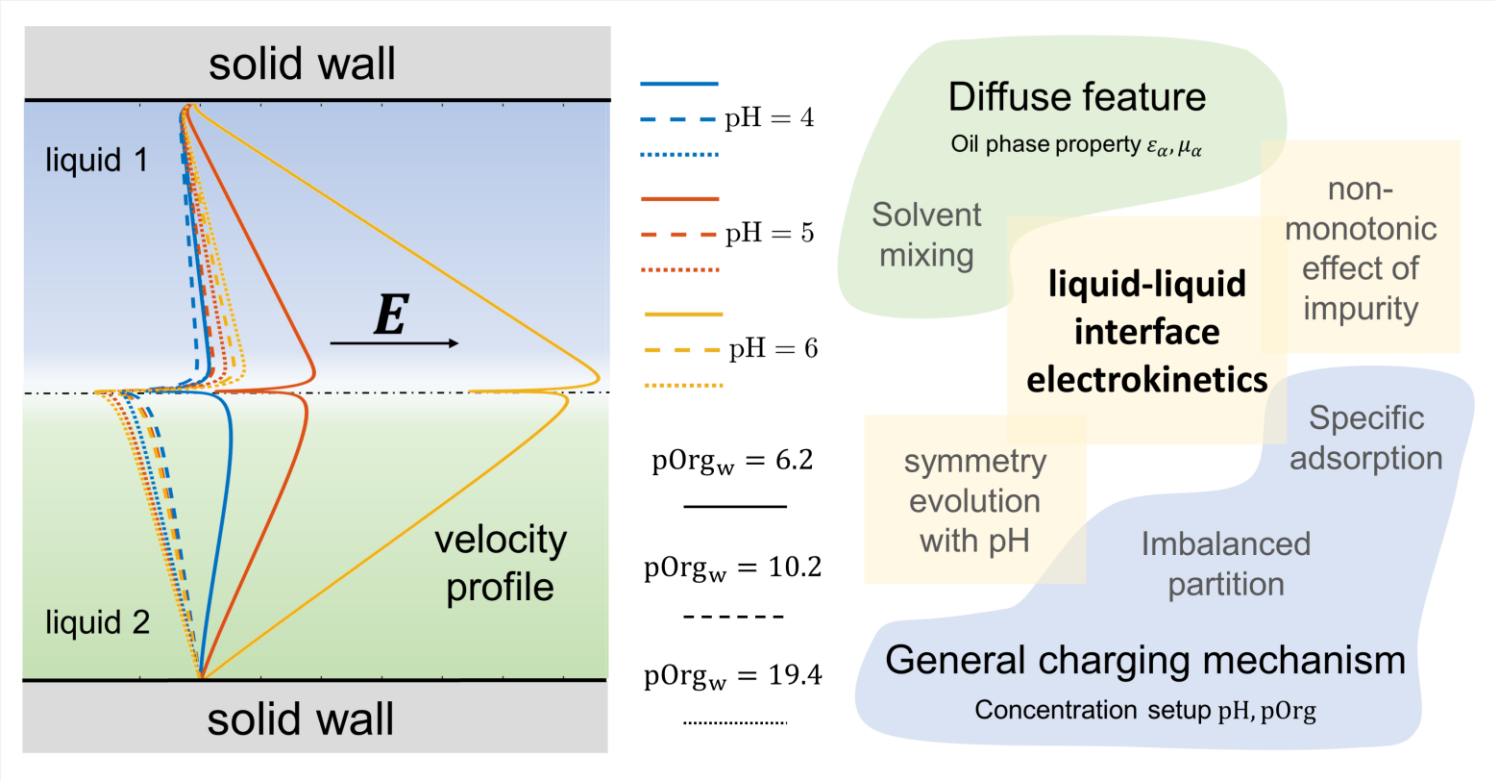
- **[Solvent mixing effect]** The potential drop across the solvent mixing layer is addressed. A **semi-empirical correction formula to account for solvent mixing effect** is given for practical utilization of sharp interface model.
  - More efforts are required to the interpretation of gas-liquid interface electrokinetics due to its essentially diffuse feature and large viscosity ratio, where phase-volume-fraction-dependent **viscosity model is demonstrated to greatly affect the interpretation**.

- **[Ion partitioning effect]** The major difference between non-polar and polar oils lies in the sensitivities to impurity ions as well as **the competition effect between the two charging mechanisms**, which is significant when permittivity ratio remains moderate.
  - The underneath mechanisms of symmetry evolution of velocity profile and non-monotonic dependency of water velocity are attributed to the **dependency of interface charging state on physico-chemical conditions such as permittivity, impurity and pH**.

Solvent mixing & ion partitioning effects in liquid-liquid interface electrokinetics

Thanks!

Questions, comments, or discussions are welcomed :-)



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Appendix: regulation of two-liquid interfacial flow by electric field

Volume forces

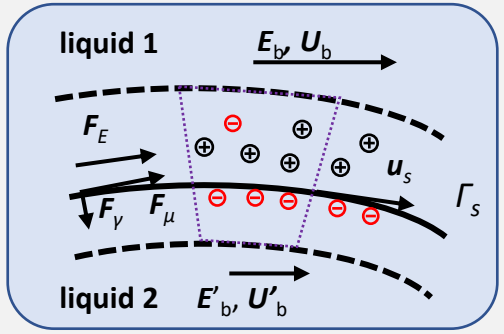
- viscous force $\mu\Delta\boldsymbol{u}$, inertial force $\boldsymbol{u}\cdot\nabla\boldsymbol{u}$
- gravity $\boldsymbol{g}$, pressure ∇p, …

Interface forces

- surface tension γ,$\nabla_s\gamma$
- disjoining pressure Π, $\nabla_s\Pi$, θ, …

Other possibilities?

Continuum electrodynamics!



Electrostatics of field and charge

$$\nabla\cdot(\varepsilon\boldsymbol{E})=\sum z_i e n_i \quad \boldsymbol{n}\times[\boldsymbol{E}]=0, \boldsymbol{n}\cdot[\varepsilon\boldsymbol{E}]=\sigma_s$$

$$\frac{\partial n_i}{\partial t}+\nabla\cdot\boldsymbol{j}_i=r_i \quad \boldsymbol{n}\cdot[\boldsymbol{j}_e]+\nabla_s\cdot\boldsymbol{j}_{e,s}=-\frac{\partial\sigma_s}{\partial t}$$

Induced-charge: Field jump | Charge flux jump !

→ **Physico-chemical (part-react-ads) origin!**

Electric force on continuum

$$\boldsymbol{F}_{e,0}=\nabla\cdot\boldsymbol{T}_e=\nabla\cdot\varepsilon\left(\boldsymbol{E}\boldsymbol{E}-\frac{1}{2}E^2\boldsymbol{I}\right)$$

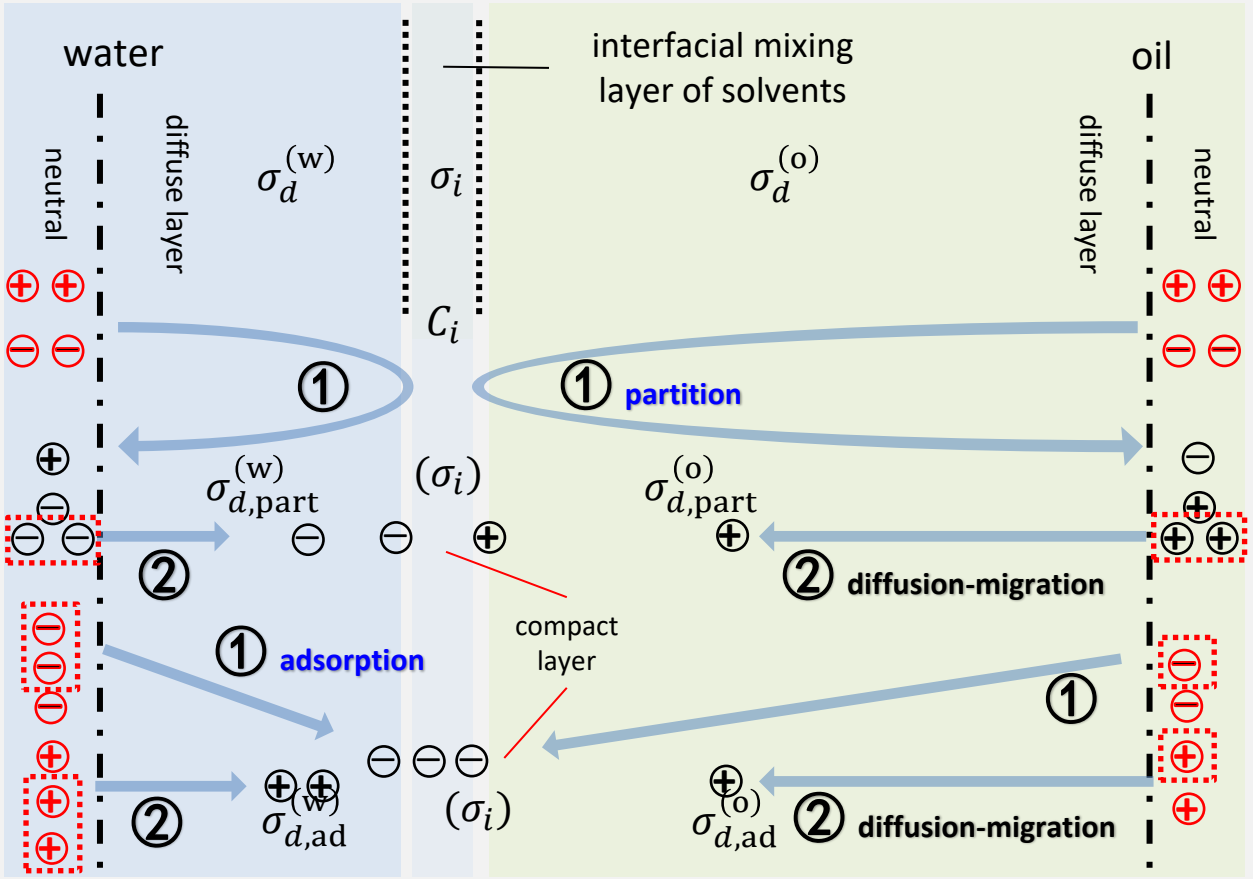
$$\boldsymbol{F}_e=\rho_e\boldsymbol{E}-\frac{1}{2}E^2\nabla\varepsilon$$

Force: Free charge | Permittivity gradient !

→ **Spontaneously charged two-liquid interface !**

Bazant. Electrokinetics meets electrohydrodynamics. *Journal of Fluid Mechanics* **782**, 1-4 (2015).

Appendix: description of two charging mechanisms of two-liquid interface



☐ ***Partition***: partition coefficient

$$\Delta_{\mathrm{w}}^{\mathrm{o}}\varphi_{\infty} \equiv \varphi_{\infty}^{\mathrm{o}} - \varphi_{\infty}^{\mathrm{w}} \simeq -\frac{\Delta_{\mathrm{w}}^{\mathrm{o}}G_{t,+} - \Delta_{\mathrm{w}}^{\mathrm{o}}G_{t,-}}{2e}$$

$$\frac{n_{+}^{\mathrm{o}}}{n_{+}^{\mathrm{w}}} = \exp\left(-\frac{\Delta_{\mathrm{w}}^{\mathrm{o}}G_{t,+} + \Delta_{\mathrm{w}}^{\mathrm{o}}G_{t,-}}{2k_{\mathrm{B}}T}\right)(\to 0)$$

☐ ***Adsorption***: surface complexation

$$> \mathrm{Y}^{\bar{s}} + \mathrm{X}^{s} \to > \mathrm{Y}^{\bar{s}} - \mathrm{X}^{s}, K_C := c_{\mathrm{X},0}c_{>\mathrm{Y}}^{\mathrm{s}}/c_{>\mathrm{XY}}^{\mathrm{s}}$$

$$\sigma_s = \sigma_{>\mathrm{Y}} + \sigma_{\mathrm{X}} = z_s e N_A\left[\frac{-c_{>\mathrm{Y,total}}^{\mathrm{s}}}{1+c_{\mathrm{X},0}/K_C} + 2d_{\mathrm{ad}}c_{\mathrm{X},0}\right]$$

$$\sigma_s^2/\varepsilon \sim \Delta\mu_d, c_{\mathrm{X},0|d} = c_{\mathrm{X},\infty}\exp\left(-\frac{z_s e\varphi_{0|d}}{k_{\mathrm{B}}T}\right)$$

Appendix: matching of evolution scale in solving CH-NS-mPNP system

- Cahn-Hilliard Navier-Stokes equation

$$\frac{\partial \phi}{\partial t} + \boldsymbol{u} \cdot \nabla \phi = \nabla \cdot \left(\chi \varepsilon_{\mathrm{pf}}^2 \right) \nabla \mu_\phi \qquad \phi = \tanh\left(\frac{D_{\mathrm{wi}}}{\sqrt{2}\varepsilon_{\mathrm{pf}}} \right)$$

$$\mu_\phi = \gamma \frac{3\varepsilon_{\mathrm{pf}}}{2\sqrt{2}} \left[-\nabla^2 \phi + \frac{(\phi^2 - 1)\phi}{\varepsilon_{\mathrm{pf}}^2} \right] \qquad d_{\mathrm{pf}} = \sqrt{2}\varepsilon_{\mathrm{pf}}$$

Dimensionless thickness of diffuse layer $\propto \frac{\lambda_{\mathrm{D}}}{L}$

Dimensionless thickness of phase interface $\propto \frac{\sqrt{2}\varepsilon_{\mathrm{pf}}}{\lambda_{\mathrm{D}}}$

- Space-time-scale matching: balance accuracy ($\downarrow d_{\mathrm{pf|ad}}$) and cost ($\uparrow d_{\mathrm{pf|ad}}$)
  - Mixing layer ($d_{\mathrm{slip}} \lesssim 1$ nm) | Double layer ($\lambda_{\mathrm{D}} \sim 10$ nm) | Flow ($L \gtrsim 100$ nm)
    - Mixing layer/ϕ: physically $d_{\mathrm{pf}} \sim d_{\mathrm{intr+fluc}} \lesssim \lambda_{\mathrm{D}}$, numerically $d_{\mathrm{pf}} \lesssim 0.1L$ and $d_{\mathrm{pf}} \ll \lambda_{\mathrm{D}}$
    - Charge/φ: physically $d_{\mathrm{pf}} \leq d_{\mathrm{ad}} \ll \lambda_{\mathrm{D}}$, numerically $d_{\mathrm{pf}} \lesssim d_{\mathrm{ad}} \lesssim 10 d_{\mathrm{pf}} \lesssim \lambda_{\mathrm{D}}$ & $\Delta_{\mathrm{i}}\varphi/\zeta \ll 1$
    - Final choice: $d_{\mathrm{ad}}/d_{\mathrm{pf}} = 1$, $\varepsilon_{\mathrm{pf}} = 0.5$ nm; slip length at contact line d_{slip}
  - Diffusion: phase field ($t_{\mathrm{pf}} = \frac{8 d_{\mathrm{pf}}}{3\gamma\chi} \sim 10^{-9}$ s) | viscosity ($t_\nu = \frac{L^2}{\nu} \sim 10^{-6}$ s) | ion ($t_{\mathrm{ion}} = \frac{\lambda_D^2}{D} \sim 10^{-8}$ s)
    - Final choice: total evolution time of phase field $T_{\mathrm{t}} = 0.01$ s

Appendix: perturbation method in solving CH-NS-mPNP system

Physical assumptions

- **Constant & uniform property, small surface charge**
  - Formulation: $\boldsymbol{F}_{\mathrm{st}} = -\phi\nabla\mu_\phi = \mu_\phi\nabla\phi - \nabla(\mu_\phi\phi) =: \mu_\phi\nabla\phi - \nabla(\Delta p_{\mathrm{st}})$
  - Ignoring: EDL polarization, surface conduction, oil streaming potential
- **Weak external electric field**
  - Formulation: $\boldsymbol{E} = -\nabla\varphi_{\mathrm{surf}} + \boldsymbol{E}_{\mathrm{ext}}^{\mathrm{ind}}$, where $\nabla\cdot\left(\sigma\boldsymbol{E}_{\mathrm{ext}}^{\mathrm{ind}}\right) = 0$
  - Ignoring: field-induced charge and electro-hydrodynamic/ wetting effect, σ_o/σ_w

$$\nabla\cdot(\varepsilon\nabla\varphi) = -\sum z_i e n_i$$

$$\frac{\partial n_i}{\partial t} + \nabla\cdot\left(n_i\boldsymbol{u} - D_i\left(\nabla n_i + n_i\nabla\ln\gamma_i^{\phi}\right) - \frac{z_i e D_i}{k_{\mathrm{B}}T}n_i\nabla\varphi\right) = 0$$

$$\nabla\cdot\boldsymbol{u} = 0, \rho\left(\frac{\partial\boldsymbol{u}}{\partial t} + \boldsymbol{u}\cdot\nabla\boldsymbol{u}\right) = -\nabla p + \nabla\cdot\mu\nabla\boldsymbol{u} + \boldsymbol{F}$$

$$\boldsymbol{F} = \mu_\phi\nabla\phi - \sum z_i e n_i\nabla\varphi - \frac{1}{2}E^2\nabla\varepsilon$$

$$\boldsymbol{r}\to\infty: \nabla\varphi = -\boldsymbol{E}_\infty, \boldsymbol{u} = \boldsymbol{u}_\infty, \bar{\bar{\sigma}}\cdot\boldsymbol{n} = \boldsymbol{0}$$

$$\boldsymbol{r}\to\infty: n_i^{(\mathrm{w})} = n_{i\infty}^{(\mathrm{w})}, \phi^{(\mathrm{w|o})} = -1|1$$

Quasi-equilibrium perturbation

$$\varphi = \tilde{\varphi}^{eq} + \delta\varphi, n_i = \tilde{n}_i^{eq} + \delta n_i$$

$$\nabla\cdot(\varepsilon\nabla\tilde{\varphi}^{eq}) = -\sum z_i e\tilde{n}_i^{eq}$$

$$\nabla\cdot\left(\nabla\tilde{n}_i^{eq} + \tilde{n}_i^{eq}\nabla\ln\gamma_i^{\phi} - \frac{z_i e\tilde{n}_i^{eq}}{k_{\mathrm{B}}T}\nabla\tilde{\varphi}^{eq}\right) = 0$$

$$0 = -\nabla p^{eq} + \boldsymbol{F}_e^{eq}$$

$$\boldsymbol{F}_e^{eq} = -\sum z_i e n_i^{\mathrm{eq}}\nabla\varphi^{eq} - \frac{1}{2}E^{eq\,2}\nabla\varepsilon$$

$$\nabla\cdot(\varepsilon\nabla\delta\varphi) = -\sum z_i e\delta n_i, \nabla\delta\varphi = -\boldsymbol{E}_\infty$$

$$\frac{\partial\delta n_i}{\partial t} + \nabla\cdot\begin{pmatrix}\tilde{n}_i^{eq}\delta\boldsymbol{u} - D_i\left(\nabla\delta n_i + \delta n_i\nabla\ln\gamma_i^{\phi}\right)\\ -\frac{z_i e D_i}{k_{\mathrm{B}}T}\left(\delta n_i\nabla\tilde{\varphi}^{eq} + \tilde{n}_i^{eq}\nabla\delta\varphi\right)\end{pmatrix} = 0$$

$$\nabla\cdot\delta\boldsymbol{u} = 0, \frac{\partial\delta\boldsymbol{u}}{\partial t} + \delta\boldsymbol{u}\cdot\nabla\delta\boldsymbol{u} = -\nabla\delta p + \nabla\cdot\mu\nabla\delta\boldsymbol{u} + \boldsymbol{F}_{\mathrm{st}} + \delta\boldsymbol{F}_e$$

$$\boldsymbol{F}_E = -\sum z_i e\left(\delta n_i\nabla\tilde{\varphi}^{eq} + \tilde{n}_i^{eq}\nabla\delta\varphi\right) - \frac{1}{2}\delta\left(E^2\right)\nabla\varepsilon$$

Two ways of simplifications: $(\delta n_i \simeq 0)$

$$\nabla\cdot(\varepsilon\nabla\delta\varphi) \simeq 0, \nabla\delta\varphi = -\boldsymbol{E}_\infty$$

$$\nabla\cdot(\sigma\nabla\delta\varphi) \simeq 0, \nabla\delta\varphi = -\boldsymbol{E}_\infty$$

Appendix: theoretical solution to sharp interface model of two-liquid EO

$$\varepsilon_\alpha \nabla^2 \varphi_\alpha = -\rho_{e,\alpha}$$

$$(\varphi_1 - \varphi_{1,\infty})\Big|_{y=d_1} = \zeta_1 \qquad (\varphi_1 - \varphi_2)\Big|_{y=0} = -\Delta_1^2 \varphi_i$$

$$(\varphi_2 - \varphi_{2,\infty})\Big|_{y=-d_2} = \zeta_2 \qquad \left(\varepsilon_1 \frac{\partial \varphi_1}{\partial y} - \varepsilon_2 \frac{\partial \varphi_2}{\partial y}\right)\Big|_{y=0} = -\sigma_s$$

Debye-Hückel approximation

$$\left(\left|\zeta_\alpha, \Delta_1^2 \varphi_\infty, \frac{\sigma_s \lambda_{D,\alpha}}{\varepsilon_\alpha}\right| \ll \zeta_T\right) \qquad \lambda_{D,\alpha}^2 \nabla^2 \tilde{\varphi}_\alpha = \tilde{\varphi}_\alpha$$

$$\varphi_{1,\infty} \equiv 0, \tilde{\varphi}_1 = \varphi_1, \tilde{\varphi}_2 = \varphi_2 - \Delta_1^2 \varphi_\infty$$

$$0 = \mu_\alpha \frac{\partial^2 u_\alpha}{\partial y^2} + \rho_{e,\alpha} E$$

$$u_1\Big|_{y=d_1} = 0, u_2\Big|_{y=-d_2} = 0, (u_1 - u_2)\Big|_{y=0} = 0$$

$$\left(\mu_1 \frac{\partial u_1}{\partial y} - \mu_2 \frac{\partial u_2}{\partial y}\right)\Big|_{y=0} = -\sigma_s E$$

$$y_\alpha = y/d_\alpha \qquad \Phi_\alpha = \tilde{\varphi}_\alpha/\zeta_T \qquad Z_\alpha = \zeta_\alpha/\zeta_T$$

$$H_\alpha = d_\alpha/\lambda_{D,\alpha} \qquad U_\alpha = u_\alpha(d_1 + d_2)/\nu_1$$

$$\Phi_1 = f_1 \frac{\cosh y_1 H_1}{\cosh H_1} + (Z_1 - f_1)\frac{\sinh y_1 H_1}{\sinh H_1}$$

$$\Phi_2 = f_2 \frac{\cosh y_2 H_2}{\cosh H_2} - (Z_2 - f_2)\frac{\sinh y_2 H_2}{\sinh H_2}$$

$$f_1 = \frac{Z_1 + \mathcal{B} Z_2/\mathcal{A}}{1+\mathcal{B}} + \left(\frac{Q_s + \mathcal{B} Z_d}{1+\mathcal{B}}\right)\cosh H_1 \qquad Q_s = \frac{\sigma_s \lambda_{D,1}}{\varepsilon_1 \zeta_T \coth H_1}$$

$$f_2 = \frac{\mathcal{B} Z_2 + \mathcal{A} Z_1}{1+\mathcal{B}} + \left(\frac{Q_s - Z_d}{1+\mathcal{B}}\right)\cosh H_2 \qquad Z_d = \frac{\Delta_1^2 \varphi_\infty - \Delta_1^2 \varphi_i}{\zeta_T}$$

$$\mathcal{A} = \frac{\cosh H_2}{\cosh H_1} \qquad \mathcal{B} = \frac{(\varepsilon_2/\lambda_{D,2}) \coth H_2}{(\varepsilon_1/\lambda_{D,1}) \coth H_1}$$

$$U_1 = U_{\mathrm{EO},1}^{(1)}(\Phi_1 - Z_1) - \frac{\mathcal{X} U_s}{1+\mathcal{X}}(1 - y_1)$$

$$U_2 = U_{\mathrm{EO},1}^{(2)}(\Phi_2 - Z_2) + \frac{U_s}{1+\mathcal{X}}(1 + y_2)$$

$$U_{\mathrm{EO},\beta}^{(\alpha)} = \frac{(\varepsilon_\alpha \zeta_T E/\mu_\alpha)(d_1 + d_2)}{\beta} \qquad \mathcal{X} = \frac{\mu_2/d_2}{\mu_1/d_1}$$

$$U_s = U_{\mathrm{EO},1}^{(1)}(\Phi_1(0) - Z_1) - U_{\mathrm{EO},1}^{(2)}(\Phi_2(0) - Z_2)$$