Demixing in electric fields gradients

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Multiphase flows with/without phase change

Zaragoza 3-4 Oct 2013

Ben Gurion University of the Negev

Map of Israel

Sea of galilee

N

City of Beer Sheva

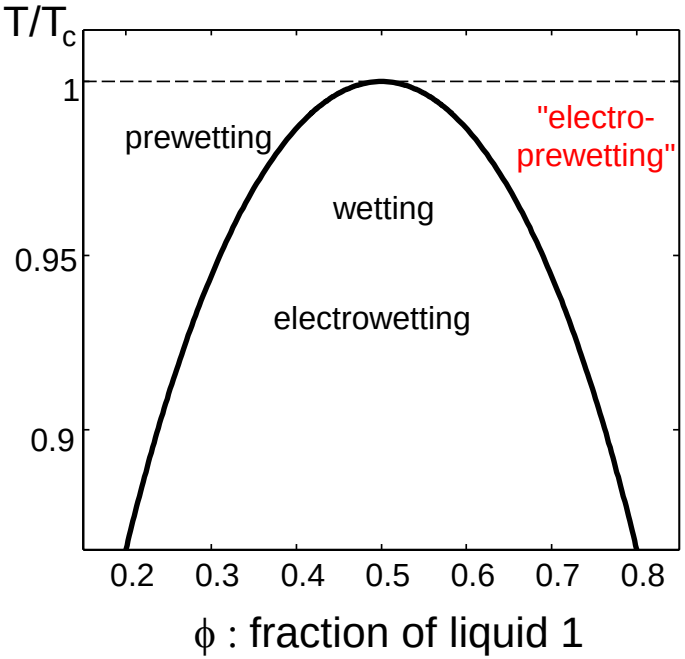
Dead sea

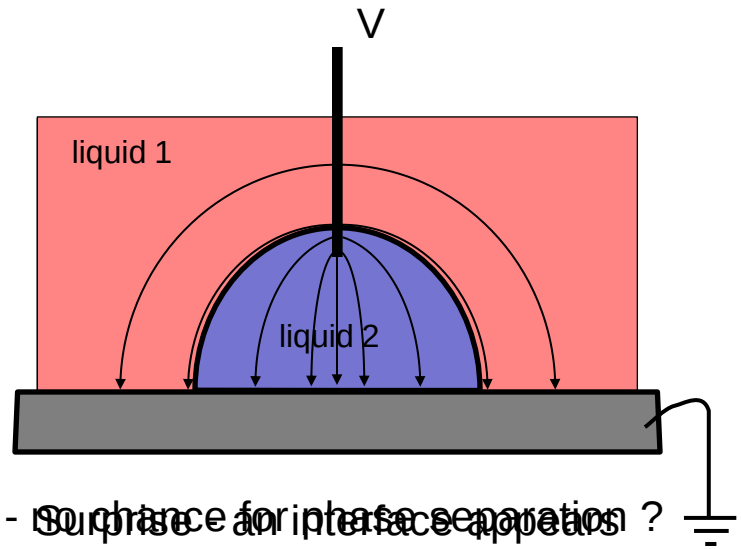
Negev region

The only place where the desert is receding

Demixing in field gradients

binary mixtures / liquid-gas coexistence





$v\varepsilon E^2 \ll k_B T$ - no chance for phase separation ?

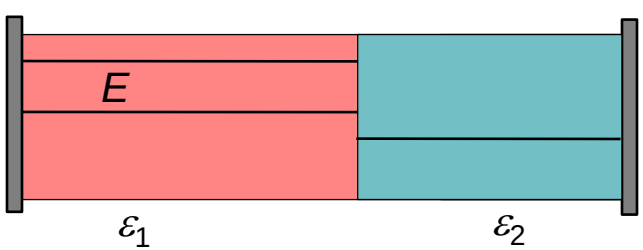
Surprise - an interface appears

<u>Electric field: a truly long range force:</u>

Field E changes density ρ

Density ρ affects E far away

} Laplace's equation $\nabla(\varepsilon(\rho)\nabla\psi) = 0$



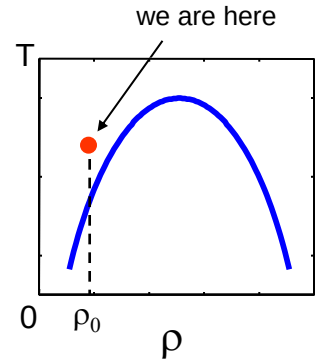
<u>"Surface tension"</u>

Displacement of the interface: energy $\propto$ volume

$\gamma\cdot$area not good !

Phase transitions in field gradients

Problem formulation



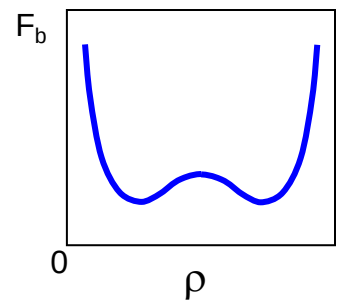
Free-energy:

$$F = F_b - \frac{1}{2}\varepsilon(\rho)(\nabla\psi)^2$$

$\psi(\boldsymbol{r})$ electrostatic potential

$\boldsymbol{E} = -\nabla\psi$ electric field

F_b bulk free energy



e.g. van der Waals:

$$F_b = k_B T\left[\log\left(\rho\Lambda^3\right) - 1 - \log(1-\rho b)\right] - a\rho^2$$

ρ : density

a, b : interaction, hard core volume parameters

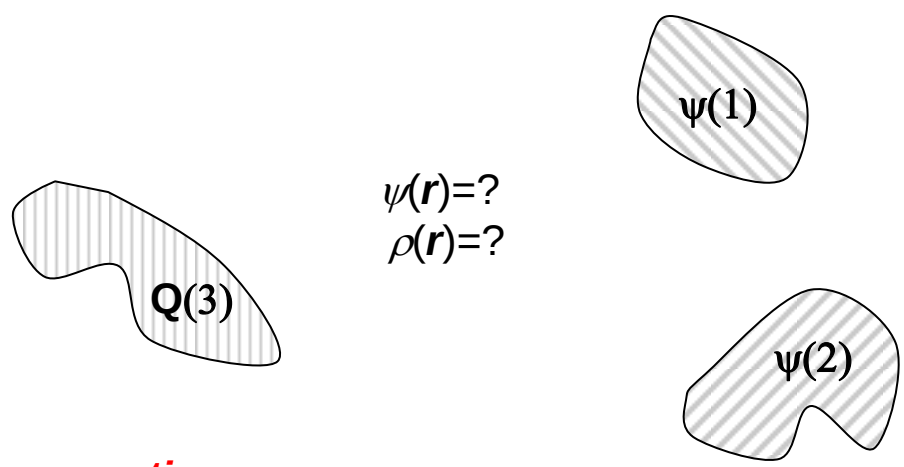
Λ : de Broglie wavelength

Equilibrium:

1) $$\frac{\delta F}{\delta\rho} = \frac{\delta F_b}{\delta\rho} - \frac{1}{2}\frac{\delta\varepsilon}{\delta\rho}(\nabla\psi)^2 - \mu = 0$$

2) $$\frac{\delta F}{\delta\psi} = \nabla\left[\varepsilon(\rho)\nabla\psi\right] = 0$$

3) $$\frac{1}{V}\int\rho(\mathbf{r})\mathrm{d}^3r = \rho_0$$



$\psi(\boldsymbol{r})$=?

$\rho(\boldsymbol{r})$=?

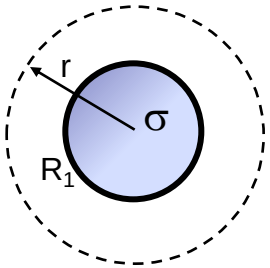
coupled nonlinear equations

Field gradients: three "canonical" systems

1) Charged colloid

$$E = \frac{\sigma}{\varepsilon(\rho)} \frac{R_1^2}{r^2}$$

$\boldsymbol{E} \parallel \nabla\rho$

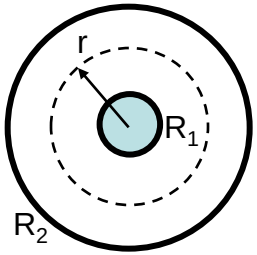


σ: surface charge density

2) Charged wire/
Concentric cylinders

$$E = \frac{\sigma}{\varepsilon(\rho)} \frac{R_1}{r}$$

$\boldsymbol{E} \parallel \nabla\rho$

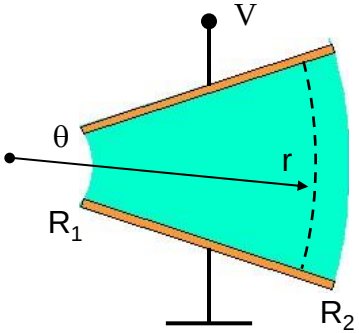


σ: surface charge density

3) Wedge

$$E = \frac{V}{\theta r}$$

$\boldsymbol{E} \perp \nabla\rho$



V: potential difference

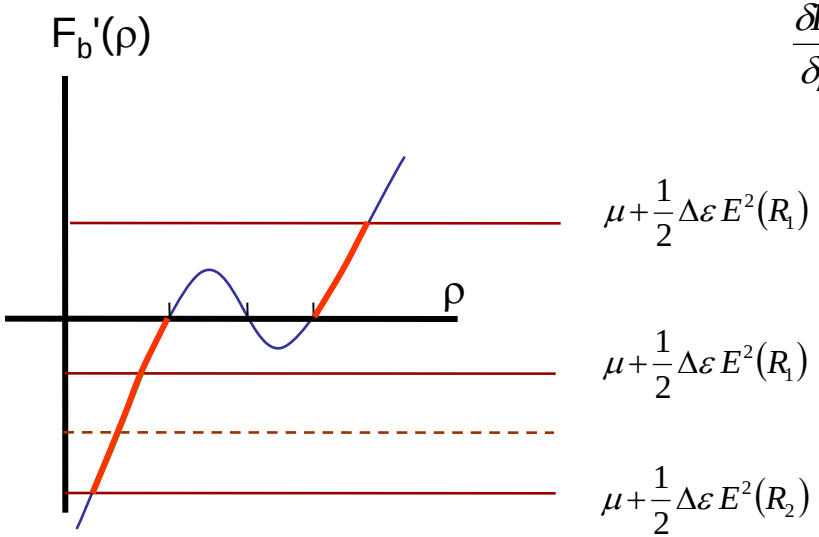
θ: opening angle

fixed charges or potentials **"open" or "closed" systems**

Field-induced phase transition

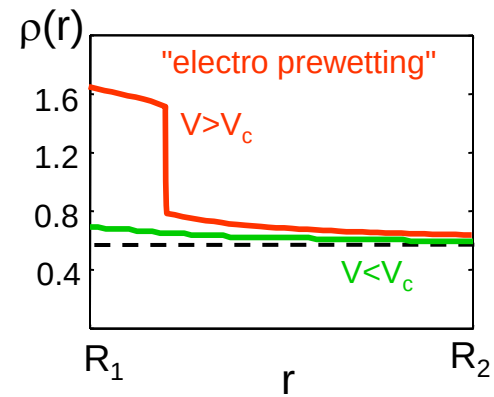
graphical solution

$$\frac{\delta F_b}{\delta \rho} = \frac{1}{2}\Delta\varepsilon \mathbf{E}^2(r) + \mu$$

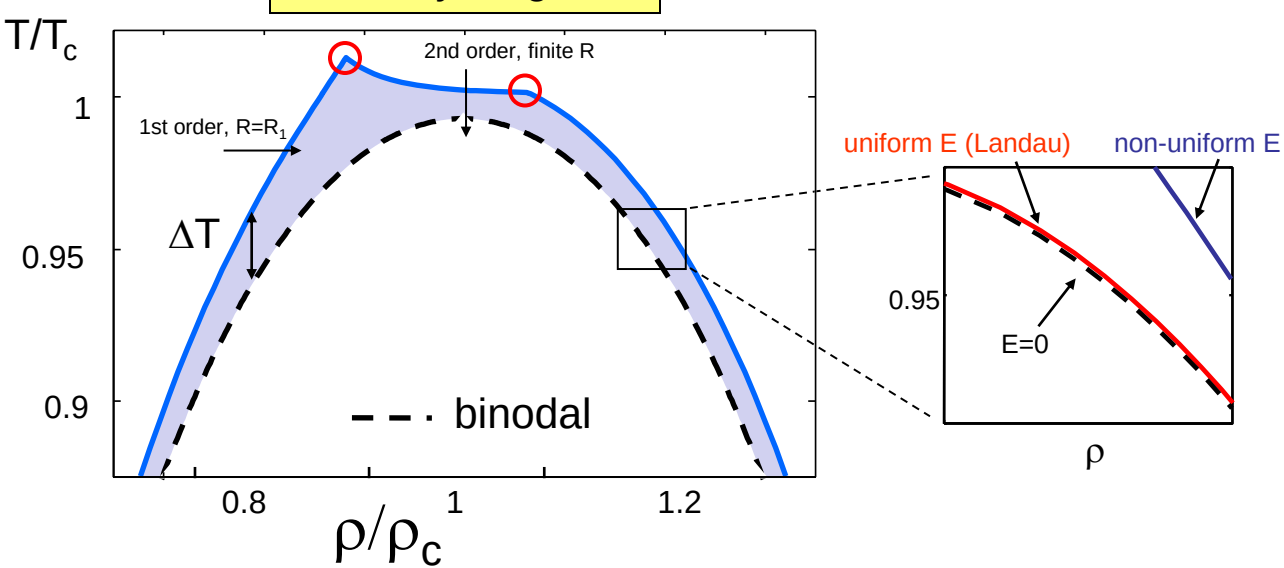


small voltage

large voltage



Stability diagram



displacement of coex. temp.:

$$\Delta T = \frac{v_0 \Delta\varepsilon}{2k_B} \frac{1}{|\rho - \rho_c|} \left(\frac{V}{\theta R_1}\right)^2$$

YT, F. Tournilhac & L. Leibler, *Nature* (2004)

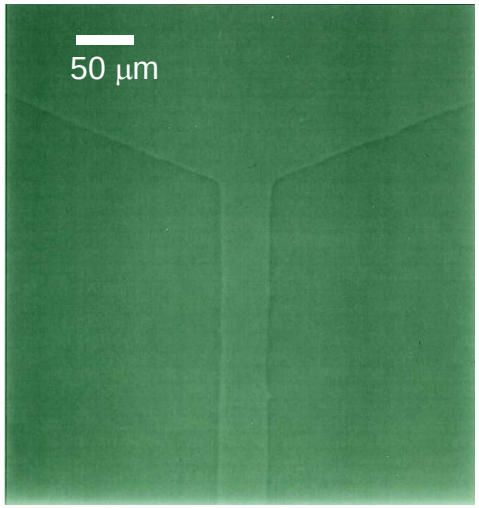
S. Samin & YT, *J. Chem. Phys.* (2009)

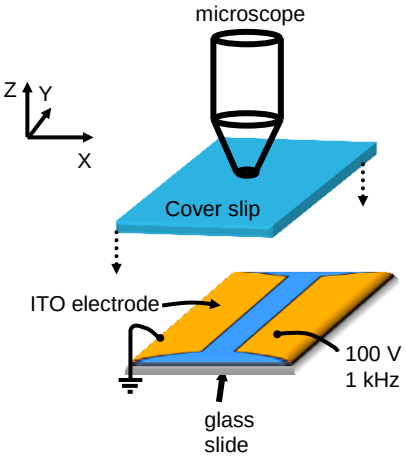
Experiments in liquid mixtures

Leibler Lab, ESPCI

V=0, $T=T_{coex}+1°C$

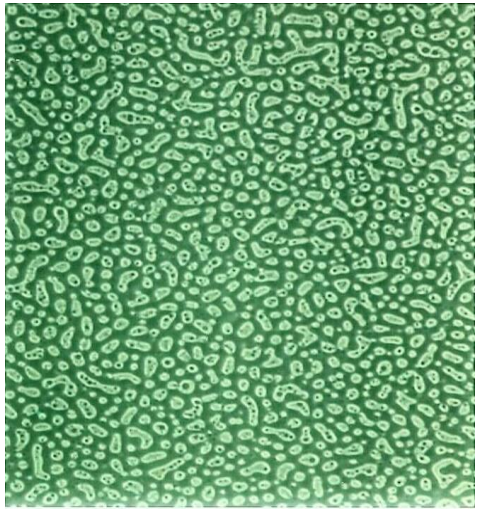
a





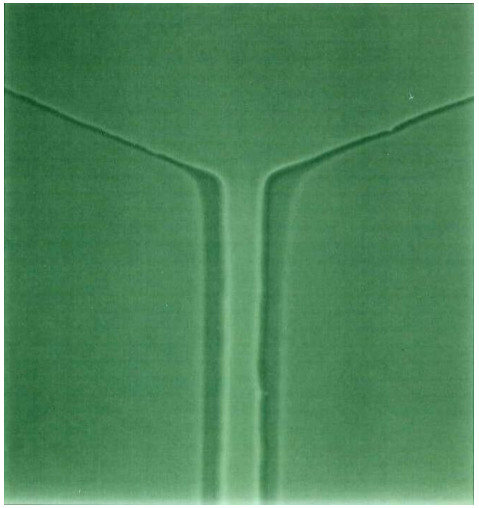
V=0, $T=T_{coex}$ -0.3°C

b



V=200V, $T=T_{coex}+0.3°C$

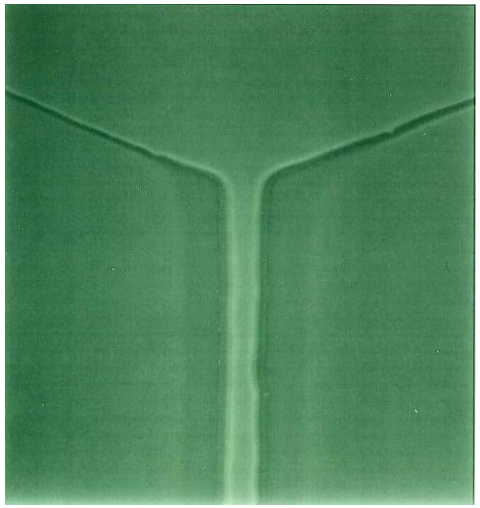
c



Liquids:
Silicon oil & Paraffin
(PMPS & Squalane)

V=300V, $T=T_{coex}+0.5°C$

d



Theoretical framework

Free energy:

$$F = F_m(\phi) - \frac{1}{2}\varepsilon(\phi)(\nabla\psi)^2 + (n^+ - n^-)e\psi + k_B T(n^+ \ln n^+ + n^- \ln n^-) + (\Delta u^+ n^+ + \Delta u^+ n^+)\phi$$

Dynamics of liquid phase separation:

$$\frac{\partial\phi}{\partial t} + \nabla(\mathbf{v}\phi) = \nabla\left(L\nabla\frac{\delta f}{\delta\phi}\right)$$

$$\nabla(\varepsilon(\phi)\nabla\psi) = 0$$

$$\nabla\mathbf{v} = 0$$

$$\rho\left[\frac{\partial\mathbf{v}}{\partial t} + (\mathbf{v}\cdot\nabla)\mathbf{v}\right] = \nabla(\eta\nabla\mathbf{v}) - \nabla P - \phi\frac{\delta f}{\delta\phi} + q(n^+ - n^+)\mathbf{E} + \frac{1}{2}\nabla\left(E^2\rho\left.\frac{\partial\varepsilon}{\partial\rho}\right|_T\right)$$

Chemical reactions:

$$\frac{d[A]}{dt} = D_A\nabla^2[A] + \frac{D_A}{kT}\nabla([A]\nabla u_A) - k[A][B]$$

$$\frac{d[B]}{dt} = D_B\nabla^2[B] + \frac{D_B}{kT}\nabla([B]\nabla u_B) - k[A][B]$$

$$\frac{d[C]}{dt} = D_C\nabla^2[C] + \frac{D_C}{kT}\nabla([C]\nabla u_C) + k[A][B]$$

$$u_A(\mathbf{r}) = u^{(1)}\phi(\mathbf{r}) + u^{(2)}(1 - \phi(\mathbf{r}))$$

Electromagnetic waves and currents:

$$\nabla\times\mathbf{E} = -\frac{\partial\mathbf{B}}{\partial t} \qquad \nabla\cdot\mathbf{D} = q(n^+ - n^-)$$

$$\nabla\times\mathbf{H} = \frac{\partial\mathbf{D}}{\partial t} + \mathbf{j}^+ + \mathbf{j}^- \qquad \nabla\cdot\mathbf{B} = 0$$

$$\frac{\partial n^\pm}{\partial t} + \nabla\cdot\mathbf{j}^\pm = 0$$

$$\mathbf{j}^\pm = n^\pm\mathbf{v} - D^\pm\nabla n^\pm \pm \mu^\pm q n^\pm\mathbf{E}$$

Temperature:

$$\rho C_p\left(\frac{\partial T}{\partial t} + \mathbf{v}\cdot\nabla T\right) = \nabla(\kappa\nabla T) + q\mathbf{j}^+\mathbf{E} - q\mathbf{j}^-\mathbf{E} + \frac{1}{2}\mu\sum_{i,j}\left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i}\right)^2$$

Numerical solutions

Electro-prewetting around a charged cylinder

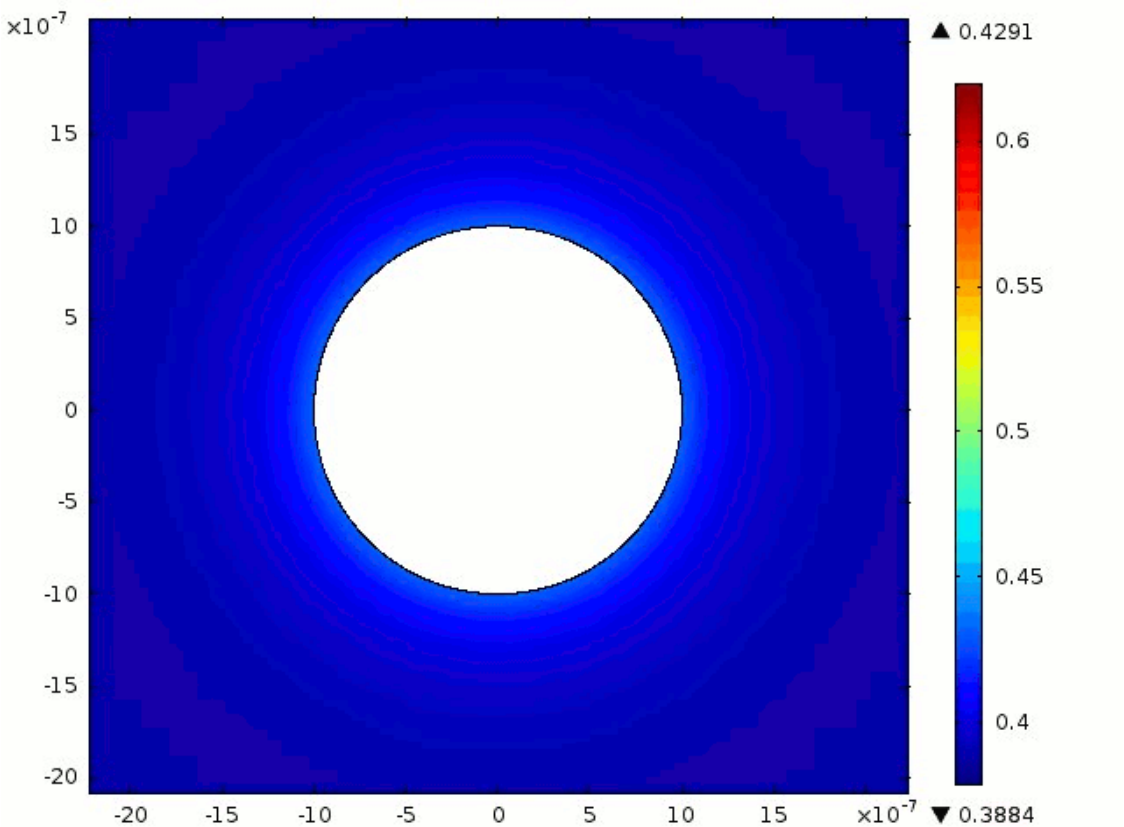
Model B dynamics:

Chemical potential: $\mu = \dfrac{\delta F(\phi,\psi)}{\delta\phi}$

Flux: $\boldsymbol{j} = -D\boldsymbol{\nabla}\mu$

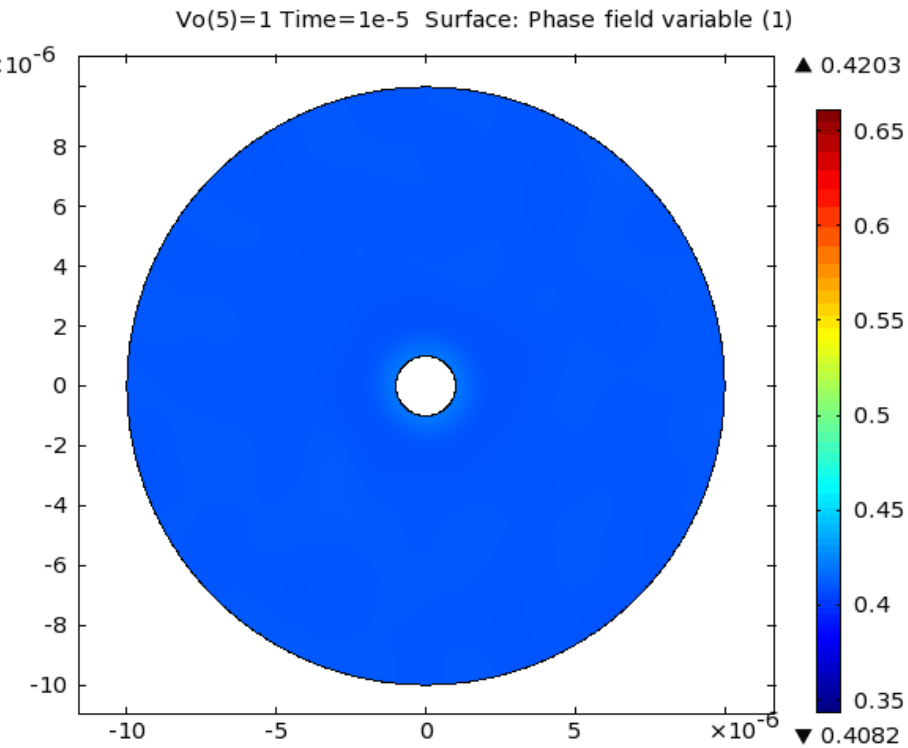
Continuity equation: $\dfrac{\partial\phi}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j} = \boldsymbol{0}$

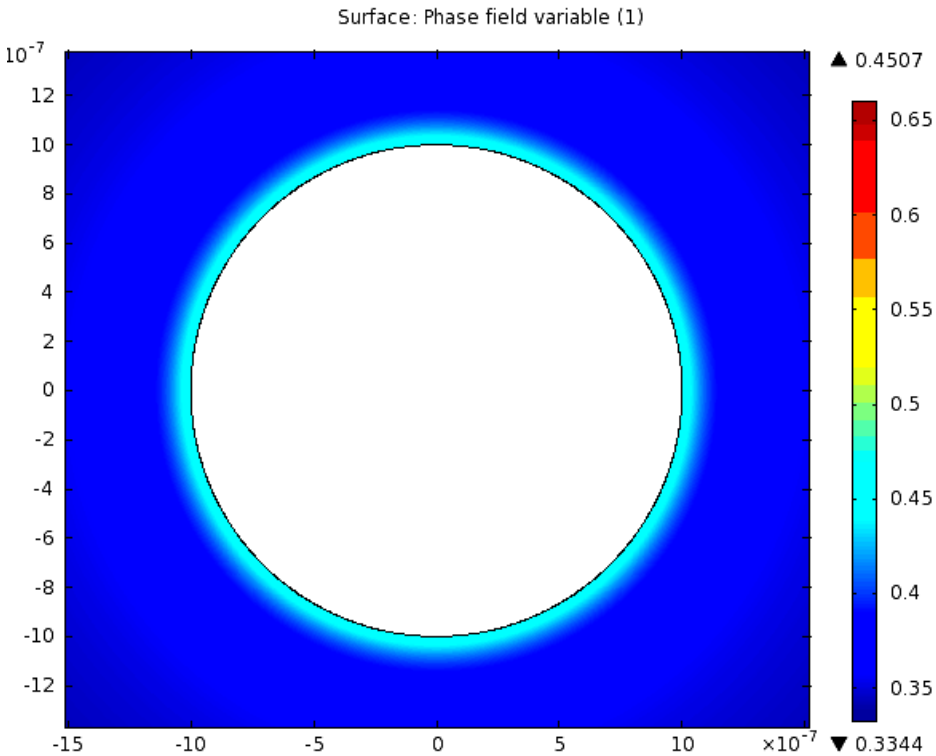
Laplace's equation: $\nabla(\varepsilon(\phi)\nabla\psi) = 0$



New interfacial instability

E-field *stabilizes* interface, surface tension *de*-stabilizes

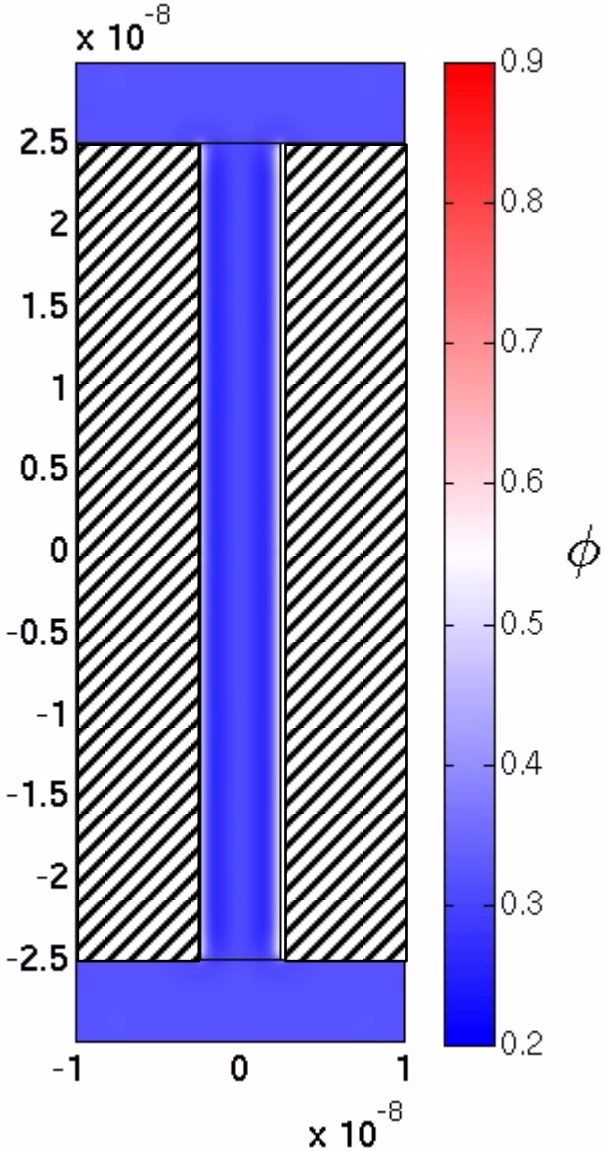




J. Galanis & YT

Pore filling

Membranes in polar mixtures



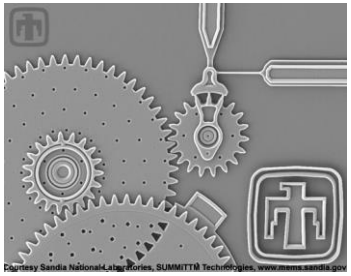
Can small molecules pass through the hole ?

homogeneous state – molecules cannot pass

Demixed state – molecules pass

Outlook – phase transitions in field gradients

- Demixing in electric field gradients: liquid-liquid and liquid-vapor coexistence
- Fascinating dynamics & interfacial instabilities
- Microfluidics of mixtures: demixing should always occur
- Electro-lubrication



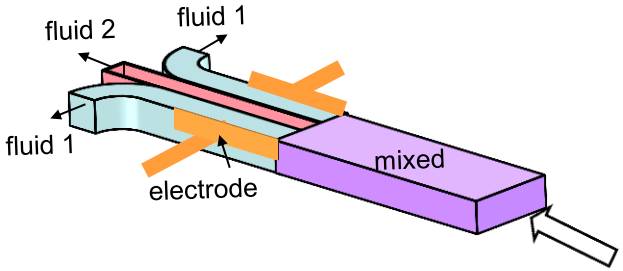
Friction becomes dominant as size shrinks

MEMS, NEMS: Charged moving parts

Field gradients → layers → huge reduction of friction

a factor of η_1/η_2 = 1500 for water/glycerol

- Demixing and additional hydrodynamic flow



"Inverse problem" of microfluidics - *how to demix ?*

Lab-on-a-chip: separate nicotine or alcohol from water

separate soluble organic solvents from polluted water

People in the group

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Thank you for your attention !