Electrical streaming potential generated by 2-phase flow

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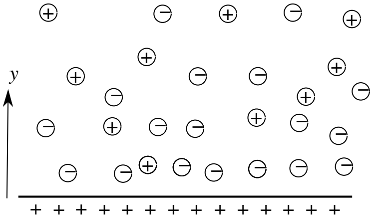
E. Lac, Schlumberger Doll Research

Electrical double layers: equilibrium



Ions above positively charged surface

Ion valence z_i, charge ez_i
Ion number density n_i
At infinity $n_i \to n_\infty^i$
Charge density $\rho = \sum_i ez_i n_i$
1–1 electrolyte: $n_\infty^+ = n_\infty^- = n_\infty$

Electrical potential ϕ
Thermal equilibrium:

$$n_i = n_\infty^i \exp\left(-\frac{ez_i\phi}{kT}\right)$$

Poisson's equation:

$$\begin{aligned}\nabla^2\phi &= -\rho/\epsilon \\ &= \sum_i \frac{ez_i n_\infty}{\epsilon} \mathrm{e}^{-ez_i\phi/kT}\end{aligned}$$

1–1 electrolyte

$$\nabla^2\left(\frac{e\phi}{kT}\right) = \frac{2e^2}{\epsilon kT}\sinh\left(\frac{e\phi}{kT}\right)$$

Electrical double layers: equilibrium (2)

If $\hat{\phi} = e\phi/kT \ll 1$, linearize:

$$\nabla^2 \phi = \sum_i \frac{e^2 z_i^2 n_\infty^i}{\epsilon kT} \phi = \kappa^2 \phi$$

where κ^{-1} is **Debye length**

$kT/e \approx 25$ mV

Wall potential ζ
Typically $e\zeta/kT < 5$

1D solution: $\phi = \zeta \mathrm{e}^{-\kappa y}$

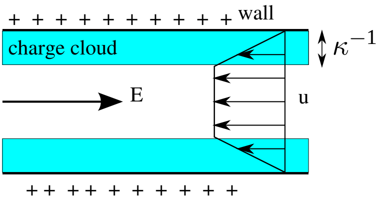
$$\rho = -\epsilon\kappa^2\phi$$
$$n^+ = n_\infty \left(1 - \frac{e\zeta}{kT}\mathrm{e}^{-\kappa y}\right)$$
$$n^- = n_\infty \left(1 + \frac{e\zeta}{kT}\mathrm{e}^{-\kappa y}\right)$$

Wall surface charge
$\sigma = -\epsilon \mathbf{n}.\nabla\phi = \epsilon\kappa\zeta$

Total charge in cloud:
$\int_0^\infty \rho \, \mathrm{d}y = -\epsilon\kappa\zeta$

Standard electrokinetic problems

Electro-osmosis



Stokes eqn:

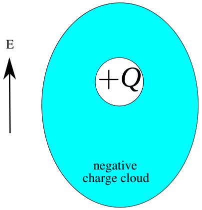
$$0 = \mu \nabla^2 \mathbf{u} - \nabla p + \rho \mathbf{E}$$

Plane 2-D channel, width $2h \gg \kappa^{-1}$

At wall $y = 0$

$$\frac{\partial^2 u}{\partial y^2} = \frac{\epsilon \kappa^2 \zeta E}{\mu} \mathrm{e}^{-\kappa y}$$

Electrophoresis

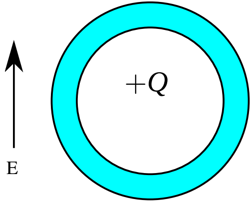


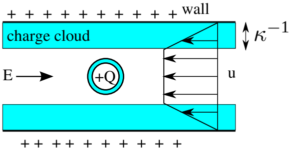
Hence

$$u = \frac{\epsilon \zeta E}{\mu} \left(\mathrm{e}^{-\kappa y} - 1 \right)$$

Electrokinetic problems (2)

Electrophoresis





Sphere (ζ_p) in capillary (ζ_c)

Thin double layer: apparent slip at wall
Electric field:

$$\nabla^2 \phi = \nabla . \mathbf{E} = 0$$

with $\mathbf{E}.\mathbf{n} = 0$ on surface of particle

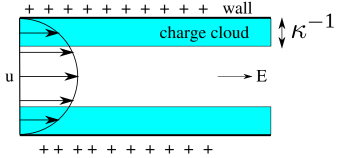
BC: $\mathbf{u}_{\text{tan}} = \mathbf{E}_{\text{tan}} \epsilon \zeta / \mu$

irrotational velocity

$$\mathbf{u} = \frac{\epsilon \zeta}{\mu} \mathbf{E}$$

Electrokinetic problems (3)

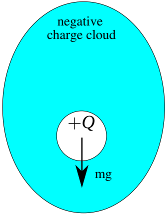
Streaming Potential



Charge cloud convected to right

Return current:
via Ohmic conduction in liquid
or some other route

Sedimentation potential



Dipole field
$\Delta\phi$ between top & bottom
of column of sedimenting
particles

Governing equations: the deformed charge cloud

Ions move under electric & thermodynamic forces

$$\mathbf{v}_i = \mathbf{u} + \omega_i(-ez_i\nabla\phi - kT\nabla \ln n^i)$$

where $\mathbf{u}$ is fluid velocity,
ω_i is ionic mobility, conductivity $\sigma = \sum_i e^2 z_i^2 n_\infty^i \omega_i$

No reactions. Conservation of ions

$$\nabla.(n^i\mathbf{v}_i) = \nabla.\left[n^i\mathbf{u} - \omega_i(ez_i n^i\nabla\phi + kT\nabla n^i)\right] = 0$$

For typical fluid velocity U and ion mobility ω
Péclet number measures ratio

$$\mathrm{Pe} = \frac{U}{\omega kT\kappa} \sim \frac{\text{convective forces}}{\text{diffusive forces}}$$

The deformed charge cloud (2)

0.1 moles/litre NaCl in water

Debye length

$$\kappa^{-1} = \left(\sum_i \frac{e^2 z_i^2 n_\infty^i}{\epsilon k T} \right)^{-1/2} \approx 1 \text{ nm}$$

Mobility $\omega = 4 \times 10^{11}$ m $\mathrm{N}^{-1}\mathrm{s}^{-1}$

Hence $\omega k T \kappa \approx 1.7$ m s^{-1}

Péclet number Pe $= U/(\omega k T \kappa) \ll 1$

In non-aqueous fluids:

Debye length larger, e.g $\kappa^{-1} = 600$ nm (Prieve 2008)

mobility smaller, e.g. $\omega = 4 \times 10^{10}$ m $\mathrm{N}^{-1}\mathrm{s}^{-1}$

Set $U = \Gamma\kappa^{-1}$ Pe $= \Gamma/(\omega k T \kappa^2)$, with $\omega k T \kappa^2 = 460\ \mathrm{s}^{-1}$

The deformed charge cloud (3)

Look for $O(\mathrm{Pe})$ perturbations

Ion density	$n^i = n_0^i + n_1^i + \cdots$
Electric potential	$\phi = \phi_0 + \phi_1 + \cdots$
Charge density	$\rho = \rho_0 + \rho_1 + \cdots$

Stokes equation: $0 = -\nabla P + \mu \nabla^2 \mathbf{u} - \rho \nabla \phi$

At $O(\mathrm{Pe})$ $\quad \mu \nabla^2 \mathbf{u}_1 = \nabla p_1 + \rho_1 \nabla \phi_0 + \rho_0 \nabla \phi_1$

if potentials small

$$\mu \nabla^2 \mathbf{u}_1 = \nabla \left(p_1 - \sum_{i=1}^{N} kT n_1^i \right) + \rho_0 \nabla (\phi_1 + \rho_1 / \epsilon \kappa^2)$$

Perturbed velocity field of magnitude

$$u_1 \sim \frac{U n_\infty}{\omega \kappa^2 \mu} \left(\frac{e\zeta}{kT} \right)^2 \sim \frac{U \epsilon \zeta^2}{\omega \mu k T}$$

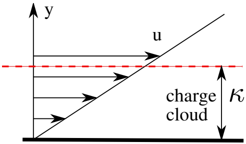
The deformed charge cloud (4)

Perturbed velocity $u_1/U = O(H)$
where electric Hartmann number

$$H = \frac{\epsilon\zeta^2}{\omega\mu kT} = \left(\frac{e\zeta}{kT}\right)^2 \frac{\epsilon kT}{\mu\omega e^2}$$

In water, $\epsilon kT/\mu\omega e^2 \approx 0.28$

Streaming potential: single phase



Convected current $I_c = \int_0^\infty \rho \mathbf{u} \, \mathrm{d}y$

Approximate $\mathbf{u}$ by $y\frac{\partial u}{\partial y}$

$$\begin{aligned} I_c &= \frac{\partial u}{\partial y} \int_0^\infty y\rho \, \mathrm{d}y \\ &= -\epsilon \frac{\partial u}{\partial y} \int_0^\infty y \frac{\mathrm{d}^2\phi}{\mathrm{d}y^2} \, \mathrm{d}y \\ &= -\zeta\epsilon \frac{\partial u}{\partial y} \end{aligned}$$

In pipe of radius R, pressure gradient $G = -8\mu Q/\pi R^4$

$$\frac{\mathrm{d}u}{\mathrm{d}r} = \frac{\mathrm{d}p}{\mathrm{d}z}\frac{R}{2\mu}$$

Convected current

$$2\pi R I_c = -\zeta\epsilon \frac{\mathrm{d}p}{\mathrm{d}z}\frac{\pi R^2}{\mu}$$

Streaming potential gradient for return current through fluid (conductivity σ)

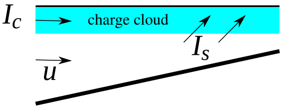
$$\frac{\mathrm{d}\phi_s}{\mathrm{d}z} = \frac{\zeta\epsilon}{\mu\sigma}\frac{\mathrm{d}p}{\mathrm{d}z}$$

Streaming potential: single phase (2)

Integrate:

$$\phi_s = \left(\frac{\zeta \epsilon}{\mu \sigma} \right) p \qquad (1)$$

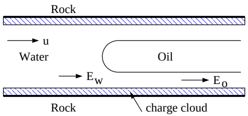
Non-uniform shear rate



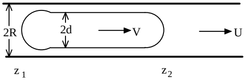
$$\nabla_s . \left(-\zeta \epsilon \frac{\partial \mathbf{u}}{\partial y} \right) = -\sigma \mathbf{n} . \nabla \phi_s$$

Suppose ζ potential uniform
All surfaces rigid, no-slip
Impose velocity $\mathbf{u}$ and pressure p
Can show (non-trivial) (1) holds for arbitrary geometry

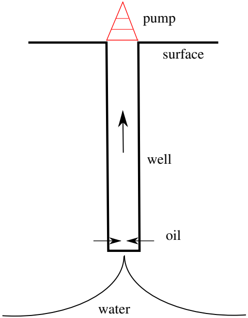
Streaming potential: two-phase



Presence of 2nd phase changes
a) wall shear rate
b) electrical conductance
c) streaming potential



Need to understand:
Pore-scale
Darcy scale
Reservoir scale

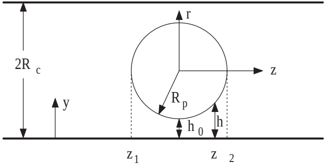


Potential difference between base of well and infinity changed by arrival of water

Need very stable electrodes

Morgan *et al.* (1989)

Tight-fitting rigid sphere



Rigid sphere, radius R_p, velocity U
Capillary radius $R_c = R_p + h_0$

Potential ζ_p on particle
ζ_c on capillary wall

lubrication theory $d = (2R_p h_0)^{1/2}$

Integral form of momentum eqn
over $z_1 < z < z_2$

in frame of particle, leakage flux

$$Q_p = -\frac{4}{3}\pi R_c h_0 U \left(1 - \frac{5h_0}{3R_c} + \cdots\right)$$

Pressure drop across sphere

$$p_1 - p_2 = p(z_1) - p(z_2) = \frac{4\pi\mu d U}{h_0 R_c}$$

Tight-fitting rigid sphere (2)

Lubrication theory for streaming potential

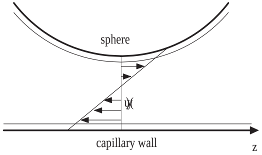
$$\phi_1 - \phi_2 = \frac{\epsilon \pi U}{2\sigma} \frac{(2R_p h_0)^{1/2}}{h_0^2} (\zeta_c - \zeta_p)$$

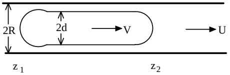
If $\zeta_c = \zeta_p$ expect

$$\phi_1 - \phi_2 = \frac{\epsilon \zeta_c}{\sigma \mu}(p_1 - p_2) = \frac{\epsilon \pi U \zeta_c}{2\sigma} \frac{16}{(2h_0 R_c)^{1/2}}$$

For uncharged stress-free bubble (spherical or Bretherton)

$$\phi_1 - \phi_2 = \frac{\epsilon \zeta_c}{\sigma \mu}(p_1 - p_2)$$





Spherical bubble:

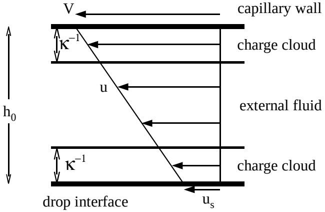
$$p_1 - p_2 = \frac{4\pi \mu U}{(2h_0 R_p)^{1/2}}$$

Bretherton bubble

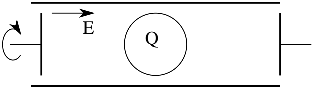
$$p_1 - p_2 = 4.81 \frac{\gamma}{R_c} \left(\frac{3\mu U}{\gamma} \right)^{2/3}$$

BCs at liquid drop/bubble

Charge at mobile interface?
Ionic surfactants
Baygents & Saville (1991)



Charged mercury drop (Ohshima *et al.* 1984)
Perfect conductor, uniform potential
No ion discharge at interface
Tangential motion of interface enhances convective flux of ions



Gas — similar problems
Spinning drop interfacial tensiometer
(JDS, JFM **162**)

Small drop in tube

Charged drop, potential ζ_d
viscosity $\mu_i = \lambda\mu$ radius a

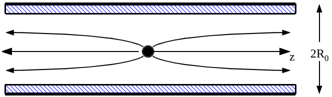
$\Delta\phi$ between tube ends:
charge cloud dipole perturbation

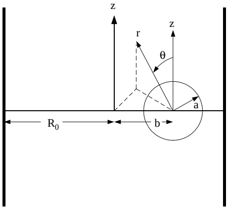
Velocity field: Hetsroni *et al.* (1970)

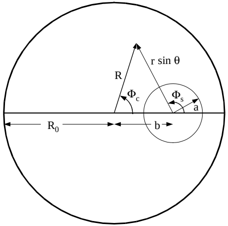
unperturbed Poiseuille flow
$v^{(0)} = \hat{\mathbf{z}}(1 - R^2/R_0^2)U_0$

Need no-slip on drop (velocity V)

add perturbation velocity $v^{(1)}$
$v^{(1)}$ fails to satisfy no-slip on capillary wall
add $v^{(2)}$ etc







Small drop in tube (2)

Thin double layer $a\kappa \gg 1$

Drop viscosity $\lambda\mu$

$$\Delta\phi = -\frac{8U_0\zeta_d\epsilon}{R_0\sigma}\left(\frac{a}{R_0}\right)^3\left[\frac{a\kappa}{2+3\lambda} + \frac{1+3\lambda}{2+3\lambda} + O(a\kappa)^{-1}\right]$$

Uncharged drop, capillary at ζ_c

Drop force free: Stokeslet $= 0$

on centreline: stresslet $= 0$

Far-field perturbation

$$u \sim \frac{U_0 a^5}{R_0^2 r^3} \qquad \sigma \sim \mu U_0 \frac{a^5}{R_0^6}$$

decays on lengthscale R_0

Additional pressure drop

$\Delta p \sim \mu U_0 a^5 / R_0^6$

Shear rate at wall $O(U_0 a^5 / R_0^2 r^4)$

Convective ion flux

$O(\epsilon\zeta U_0 a^5 / R_0^2 r^4)$

Current normal to wall

$O(\epsilon\zeta U_0 a^5 / R_0^2 r^5)$

Integrate once to get change in axial current

Integrate again

$$\Delta\phi \sim \frac{\epsilon\zeta U_0}{\sigma R_0}\left(\frac{a}{R_0}\right)^5$$

Small drop in tube (3)

Electric field when no drop: $E = 4U_0\epsilon\zeta_c/R^2\sigma$
Dipole perturbation due to insulating drop

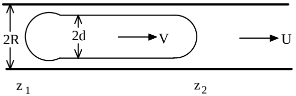
$$\phi = -\left(1 + \frac{a^3}{2r^3}\right)\mathbf{E}.\mathbf{r}$$

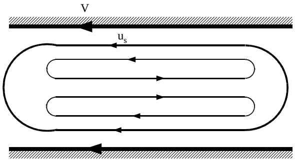
Streaming potential change

$$\Delta\phi = \frac{8U_0\zeta_c}{\sigma R_0}\left(\frac{a}{R_0}\right)^3 = \frac{16U\zeta_c}{\sigma R_0}\left(\frac{a}{R_0}\right)^3$$

where $U = U/2$ is average flow rate

Viscous Bretherton drop





Drop viscosity $\lambda\mu$
Interfacial tension γ

Capillary number
$\mathrm{Ca} = \mu U/\gamma$

Fluid (mean) velocity U
Drop velocity V

Drop cylindrical radius $d = \delta R = R - h$
Drop volume $4\pi a^3/3 = 4\pi(\alpha R)^3/3$
Drop length $L \approx 4a^3/3d^2$

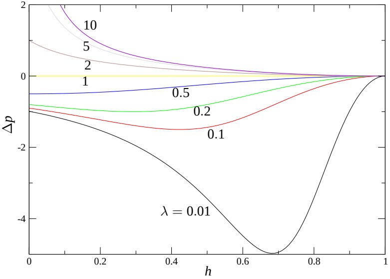
Bretherton: $h = 1.337 R\,\mathrm{Ca}^{2/3}$
valid $\lambda \ll Ca^{-1/3}$ Park & Homsy (1984)

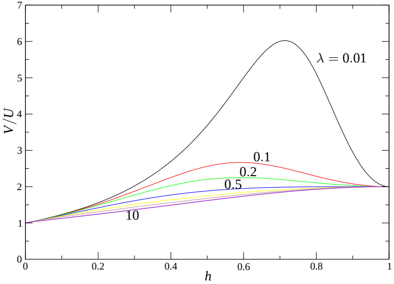
Hodges *et al.* (2004) for higher viscosity

Continuity of stress & velocity

$$\frac{R^2}{\mu}\frac{\mathrm{d}p}{\mathrm{d}z} = -\frac{8U}{1 + \delta^4(\lambda^{-1} - 1)}$$

Viscous Bretherton drop (2)





Δp = pressure increase due to drop

V = drop velocity

$$\left(\frac{3R^4}{32Ua^3\mu}\right)\Delta p = -\frac{\delta^2(\lambda^{-1}-1)}{1+\delta^4(\lambda^{-1}-1)}$$

$$\frac{V}{U} = \frac{2+\delta^{(}\lambda^{-1}-2)}{1+\delta^4(\lambda^{-1}-1)}$$

Viscous Bretherton drop (3)

Change in streaming potential caused by uncharged drop

$$\Delta\phi = \frac{32U\epsilon\zeta_c a^3}{3R^4\sigma}\frac{1+(\delta^4-\delta^2)(\lambda^{-1}-1)}{(1-\delta^2)[1+\delta^4(\lambda^{-1}-1)]}$$

$\Delta\phi = 0$ when

$$2\delta^2 = 1 \pm \left(1 - \frac{4}{\lambda^{-1}-1}\right)^{1/2}$$

real roots if $\lambda \leq 1/5$

Change in potential above that expected for pressure change

$$\Delta\phi - \frac{\epsilon\zeta_c\Delta p}{\mu\sigma} = \frac{32U\epsilon a^3\zeta_c}{3R^4\sigma(1-\delta^2)[1+\delta^4(\lambda^{-1}-1)]}$$

Viscous Bretherton drop (4)

$$\frac{V}{U} = \frac{2+\delta^2(\lambda^{-1}-2)}{1+\delta^4(\lambda^{-1}-1)}$$

Expand for $\delta \ll 1$

$$\begin{aligned} V - 2U &= -\delta^2(2-\lambda^{-1})U \\ &\quad -2\delta^4(\lambda^{-1}-1)U + O(\delta^6 U) \end{aligned}$$

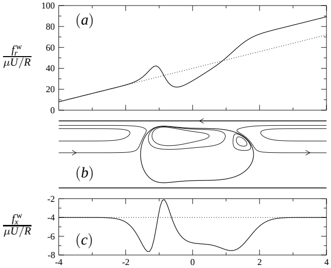
$V < 2U \quad \text{if } \lambda > 1/2$

Normal stress balance

$$\mu\frac{V-2U}{R} \sim \frac{\gamma}{R\delta}$$

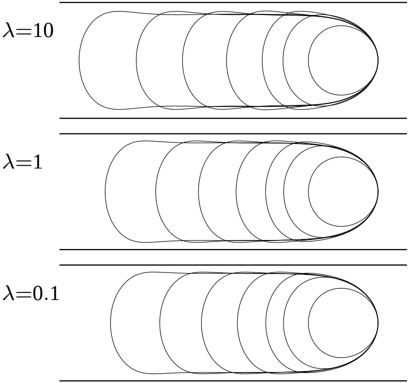
Hence

$$\begin{aligned} \delta &\sim (2-\lambda^{-1})^{-1/3}\mathrm{Ca}^{-1/3} \qquad \lambda > 1/2 \\ &\sim \mathrm{Ca}^{-1/5} \qquad \lambda = 1/2 \end{aligned}$$



a) wall normal stress
b) steady drop
c) wall shear stress
$\alpha = 1.1, \quad \mathrm{Ca} = 0.05$
$\lambda = 10$

Boundary integral computations

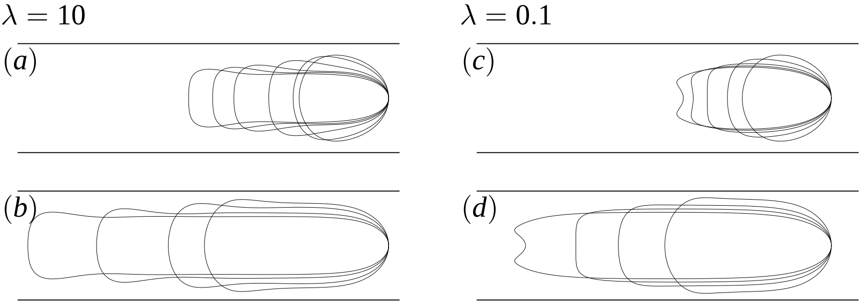


Steady drop profiles

Ca=0.05 $\lambda = 0.1, 1, 10$

Drop volume $\frac{4}{3}\pi a^3$ $\alpha = a/R = 0.6, 0.8, [0.1], 1.3$

Boundary integral computations (2)



Steady drop profile at increasing capillary number

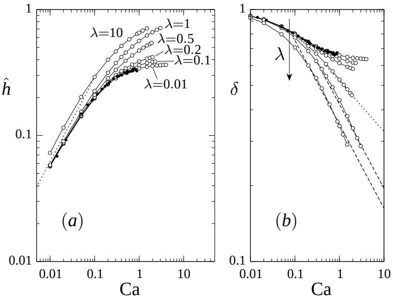
(a) $\lambda = 10$, $\alpha = 0.8$, $\mathrm{Ca} = 0.05, 0.1, [0.1], 0.5$

(b) $\lambda = 10$, $\alpha = 1.1$, $\mathrm{Ca} = 0.05, 0.1, 0.2, 0.3$

(c) $\lambda = 0.1$, $\alpha = 0.8$, $\mathrm{Ca} = 0.05, 0.2, 0.5, 1, 2$

(d) $\lambda = 0.1$, $\alpha = 1.1$, $\mathrm{Ca} = 0.05, 0.2, 0.5, 2.35$

BI computations: gap width $h = 1 - d$



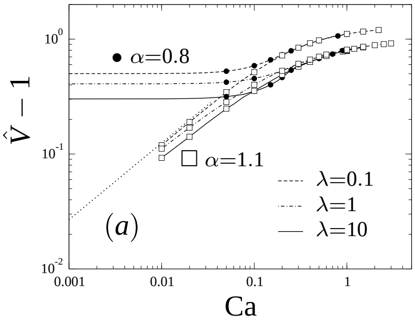
(a) Film thickness $\hat{h} = h/R$ *vs.* Ca

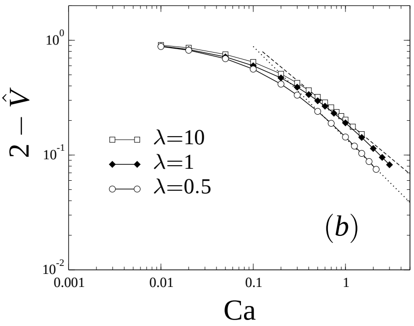
dotted:
Bretherton $\hat{h} \approx 1.3375\,\mathrm{Ca}^{2/3}$

(b) drop breadth $\delta = 1 - \hat{h}$ *vs.* Ca
same λ as in (a)

dashed $\sim \mathrm{Ca}^{-1/3}$
dotted $\sim \mathrm{Ca}^{-1/5}$
• experiments Taylor (1961)

BI computations: velocity





(a) Drop velocity $\hat{V} = V/U$ *vs.* Ca for $\lambda = 0.1, 1, 10$

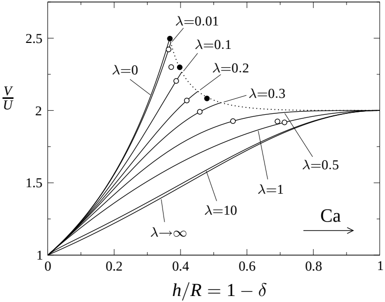
• $\alpha = 0.8$ □ $\alpha = 1.1$

Dotted: Bretherton bubble, $\hat{V} \approx 1 + 1.29\,(3\,\mathrm{Ca})^{2/3}$

(b) $2U - V$ for $\alpha = 1.1$ and $\lambda \geqslant 0.5$

dashed $\sim \mathrm{Ca}^{-2/3}$ dotted $\sim \mathrm{Ca}^{-4/5}$

BI computations: velocity (2)



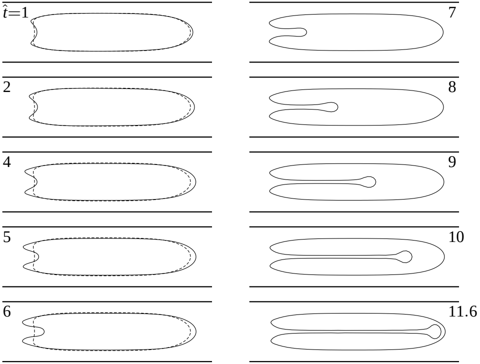
V/U *vs.* film thickness h
Dotted: approximate limit values of h and V for $\lambda < 0.5$

$$\delta_\infty^2 = \frac{2}{5}\left(\frac{1-2\lambda}{1-\lambda}\right)$$

$\circ$ last point for drop $\lambda \leqslant 1$

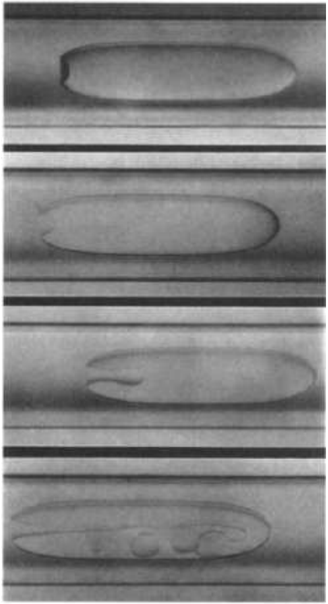
$\bullet$ Soares *et al.* (2005)
infinite finger, Ca $\gg 1$
$\lambda^{-1} = 10^3, 12, 4$

BI computations: instability

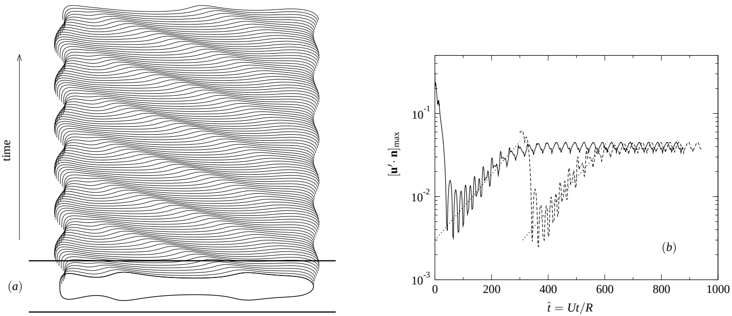


Breakup of low-viscosity drop, $\lambda = 0.1$
$\alpha = 1.1$
Ca increased from 1 to 2 at $\hat{t} = tU/R = 0$
dashed : steady drop profile at Ca $= 1$

Experiments: Olbricht ($\lambda = 0.0013$?)
Annual Rev. Fluid Mech. **28** (1996) 187



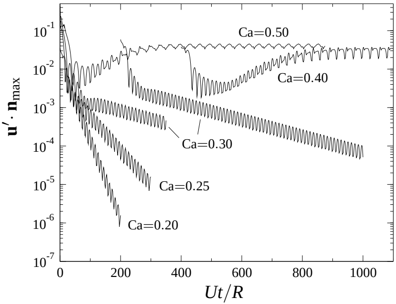
BI computations: instability (2)



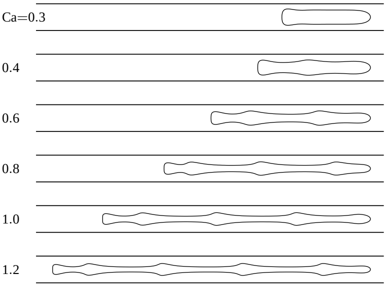
Travelling wave instability, in centre-of-mass frame
$\lambda = 10$, $\alpha = 1.1$, $\mathrm{Ca} = 0.5$
Capillary wall shown on first (bottom) profile

(b) maximum normal velocity $(\mathbf{u}'.\mathbf{n})_{\mathrm{max}}$ on drop surface
solid line: $N = 100$, $\Delta\hat{t} = 0.005$
dashed: $N = 160$, $\Delta\hat{t} = 0.002$

BI computations: instability (3)



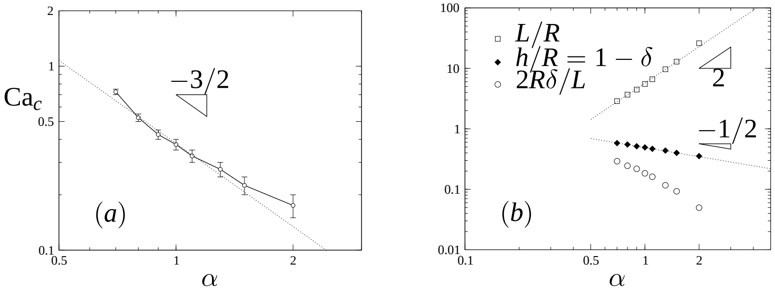
Maximum normal velocity,
$\lambda = 10$, $\alpha = 1.1$
Various Ca, started from steady state at lower Ca



Drop profiles $\lambda = 10$, $\alpha = 1.1$
Only Ca $= 0.3$ is steady

Kuramoto-Sivashinsky eqn
Papageorgiou *et al.* (1990)

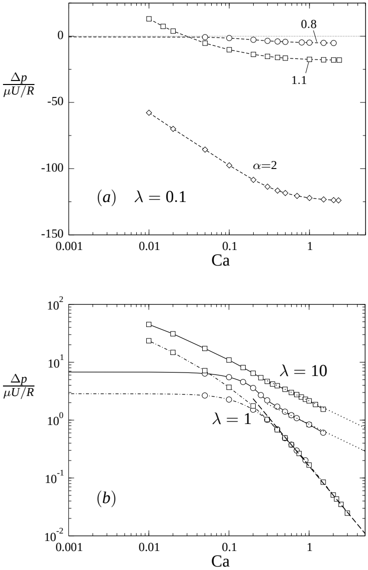
BI computations: instability (4)



Critical capillary number Ca_c
vs drop size $\alpha = a/R$
$\lambda = 10$
error bars:
last stable and first unstable Ca

drop length L
film thickness h
slenderness ratio $2R\delta/L$
at last stable Ca

BI computations: pressure



Additional pressure drop Δp *vs.* Ca

$\circ\ \alpha = 0.8$ $\square\ \alpha = 1.1$ $\diamond\ \alpha = 2$

(a) $\lambda = 0.1$ (dashed)

(b) $\lambda = 1$ (dot-dash) $\lambda = 10$ solid

Drop length (spherocylinder)

$l = \frac{4}{3}(a^3 - d^3)/d^2$

Increase in pressure due to drop

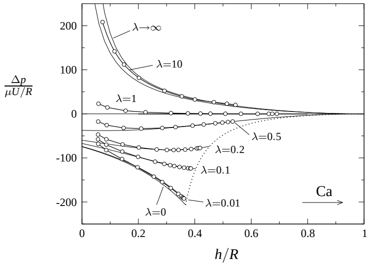
$$\frac{\Delta p}{\mu U/R} \sim \alpha^3 (1-\lambda^{-1})(2-\lambda^{-1})^{-2/3} \mathrm{Ca}^{-2/3}$$

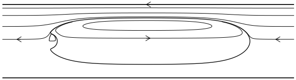
dotted lines $\sim \mathrm{Ca}^{-2/3}$

$\lambda = 1$: end caps $R\Delta p/\mu U \sim \mathrm{Ca}^{-5/3}$

thick dashed line $\sim \mathrm{Ca}^{-5/3}$

BI computations: pressure (2)





$\lambda = 0.01$, $\alpha = 1.1$, $\mathrm{Ca} = 3.5$

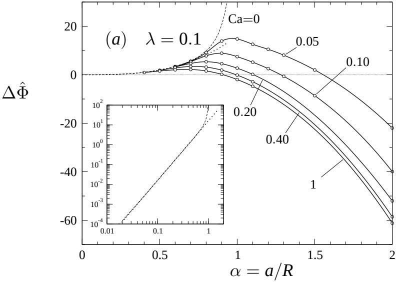
Additional pressure drop Δp *vs.* film thickness h ($\alpha = 2$)
Thin lines: asymptote

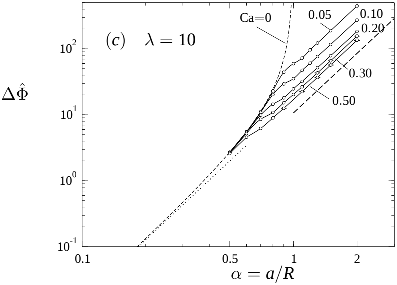
$$\frac{\Delta p^{(\mathrm{cyl})}}{\mu U/R} \approx -\frac{32}{3} \frac{(1-\lambda)\,\delta^2}{\lambda + (1-\lambda)\,\delta^4} (\alpha^3 - \delta^3)$$

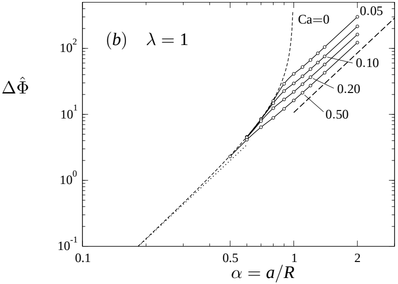
$\circ$ numerical results
Dotted: approximate limit film thickness ($\lambda < 1/2$)

$$\delta_\infty^2 = \frac{2}{5}\left(\frac{1-2\lambda}{1-\lambda}\right)$$

Streaming potential $\Delta\hat{\Phi} = \Delta\Phi(\sigma R/\epsilon\zeta_c U)$ *vs.* drop size





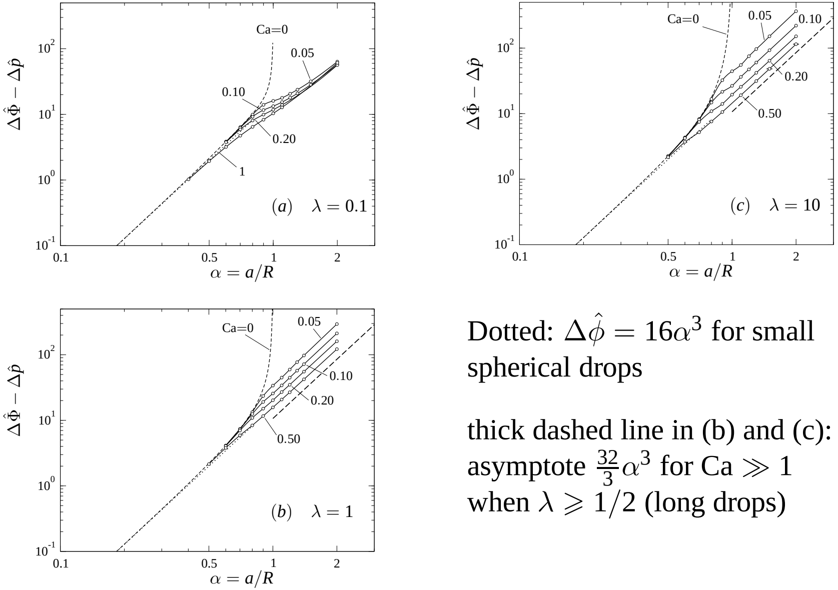


Wall potential ζ_c
$\lambda = 0.1, 1, 10$

Dotted line: $\Delta\hat{\phi} = 16\alpha^3$ for small spherical drops

thick dashed line in (b) and (c): asymptote $\frac{32}{3}\alpha^3$ for Ca $\gg 1$ when $\lambda \geqslant 1/2$ (long drops)

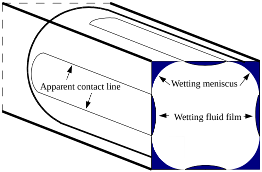
$\Delta\hat{\Phi} - \Delta\hat{p} = \Delta\Phi(\sigma R/\epsilon\zeta_c U) - \Delta p(R/\mu U)$

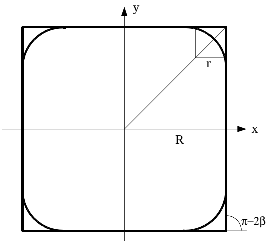


Dotted: $\Delta\hat{\phi} = 16\alpha^3$ for small spherical drops

thick dashed line in (b) and (c): asymptote $\frac{32}{3}\alpha^3$ for Ca $\gg 1$ when $\lambda \geqslant 1/2$ (long drops)

Polygonal capillary





Modern network simulators for 2-phase flow in porous media use polygonal capillaries (e.g. Blunt)

Films of wetting fluid (Wong, Morris & Radke 1995)
Thickness $h \sim O(\mathrm{Ca}^{2/3})$ varies downstream and across capillary

If $h \gg \kappa^{-1}$
convected ionic current computed from integral of shear rate
Ohmic return current mainly through corners

Future

Theory now ahead of experiment

Have not discussed: high potentials
Hartmann number
surface conduction at wall

Yet to understand:

1. Limiting film thickness for $\lambda < 1/2$
2. Onset of capillary wave instability
3. Electrokinetics at oil/rock interface
4. Electrokinetics at water/oil interface
5. Flow through constrictions
6. Scale up from pore to Darcy scale

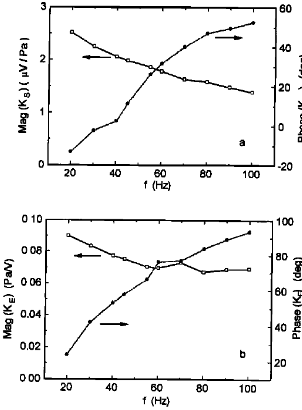


Fig. 1. Frequency dependence of streaming potential (a) and electro-osmosis coefficient (b) when the porous rock is saturated with transformer oil.

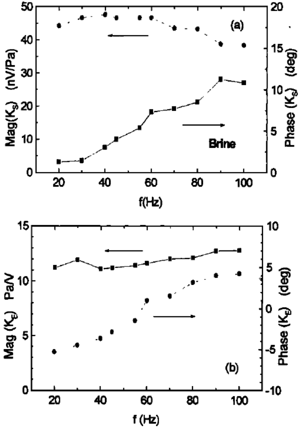


Fig. 2. As figure 1 but saturated with 0.1 mole brine.

Jiang, Shan, Jin, Zhou & Sheng, *Geophys. Res. Lett.* **25** (1998) 1581

Effect of conductivity σ: $\Delta\phi = (\epsilon\zeta/\sigma\mu)\Delta p$

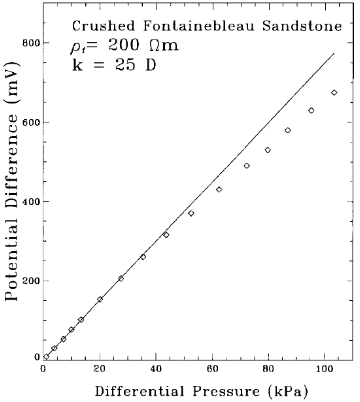


Figure 4. The streaming potential as a function of the applied pressure gradient. The maximum pressure gradient used for the measurements of streaming potentials at this permeability was 30 kPa.

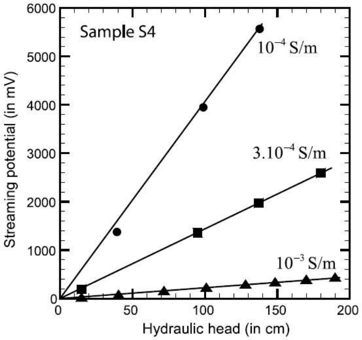


Figure 3. Example of typical runs for sample S4 (grain size of 212–300 μm) at three water conductivities. We observe linear relationships between the variation of the streaming potentials and the variation of the hydraulic heads at these different salinities. At each salinity, the streaming potential coupling coefficient is equal to the slope of the linear trend.

Lorne, Perrier & Avouac, *J. Geophys. Res.* **B104** (1999) 17857

Bolève, Crespy, Revil, Janod & Mattiuzzo, *J. Geophys. Res.* **B112** (2007) B08204

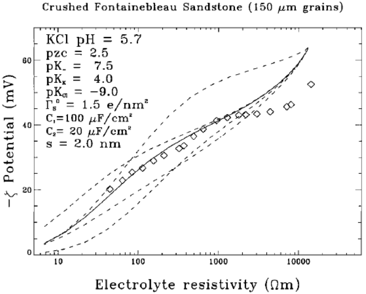


Figure 7. The ζ potential, inferred from streaming potential measurements using crushed Fontainebleau sandstone, as a function of electrolyte resistivity for KCl solutions with pH = 5.7. The measurement experimental errors are of the size of the symbols. The lines correspond to the predictions of the three-layer model [*Davis et al.*, 1978]. The solid line correspond to the default parameters indicated. The dotted line refers to the related Stern plane potential. The dashed lines correspond to pK_{K^+} increased or decreased by 1. When K_{K^+} is increased, the absolute value of the ζ potential is decreased. The dash-dotted lines correspond to pK_{Cl} increased or decreased by 1. When K_{Cl} is increased, the absolute value of the ζ potential is increased.

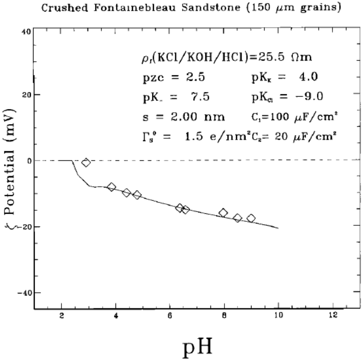


Figure 11. The ζ potential, inferred from streaming potential measurements using crushed Fontainebleau sandstone, as a function of pH for KCl/HCl/KOH solutions with a resistivity of 25.5 Ω m. The measurement experimental errors are of the size of the symbols. The lines correspond to the predictions of the three-layer model [*Davis et al.*, 1978]. The solid line corresponds to the default parameters indicated. The dotted line refers to the related Stern plane potential.

Lorne, Perrier & Avouac, *J. Geophys. Res.* **B104** (1999) 17857