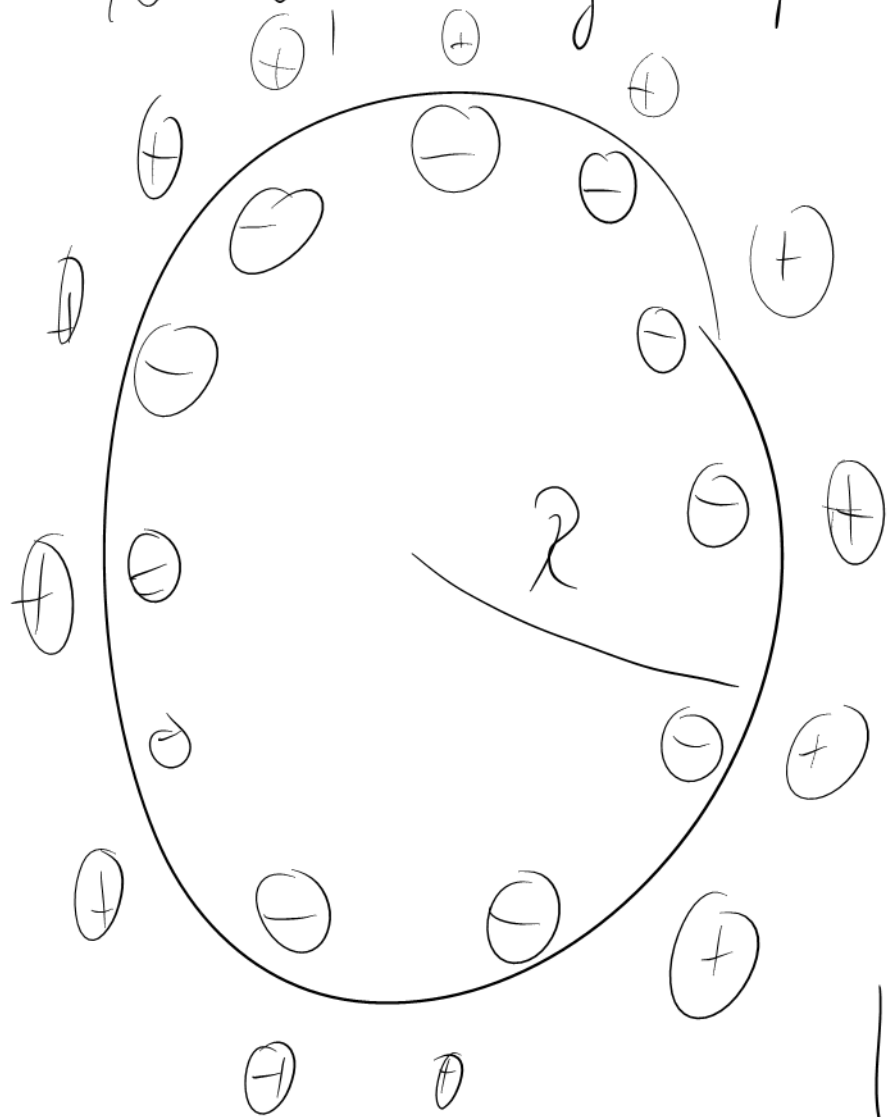


Now, study a sphere fixed in space



$$\vec{E}_{\text{ext}} \propto \hat{e}_z$$

average flow in the direction of \vec{E}_{ext}

System is strongly screened

$$KR \gg 1$$

locally: geometry is planar \sim results of

electro-osmosis can be (in principle) transferred

EKE: $\vec{\nabla} \cdot \vec{v} = 0$

$$-\vec{\nabla} p + \eta \vec{\nabla}^2 \vec{v} - \sum_a z_a e c_a \vec{\nabla} \phi = 0$$
$$\vec{\nabla} \cdot \left\{ -D_a \vec{\nabla} c_a - \frac{D_a}{k_B T} z_a e c_a \vec{\nabla} \phi + c_a \vec{v} \right\} = 0$$

$$\left\{ \vec{\nabla}^2 \phi + \sum_a z_a e c_a \right\} = 0$$

$\vec{\nabla} c_a \neq 0$ only near surface. But there $\vec{v} \parallel$ surface,

and $\vec{\nabla} c_a \perp$ surface \Rightarrow

$$\vec{\nabla} \cdot (c_a \vec{v}) = c_a \underbrace{\vec{\nabla} \cdot \vec{v}}_{=0} + \underbrace{(\vec{\nabla} c_a) \cdot \vec{v}}_{=0} = 0$$

~ Nerst-Planck:

$$\vec{\nabla} \cdot \left[-\vec{\nabla} c_a - \frac{1}{k_B T} z_a e c_a \vec{\nabla} \phi \right] = 0$$

perturbation theory: expansion parameter $\phi \ll 1$
 $\propto E_{ext}$

1st order

$$C_a = C_a^{(0)} + \varphi C_a^{(1)} + \varphi^2 C_a^{(2)} + \dots$$

$$\Phi = \Phi^{(0)} + \varphi \Phi^{(1)} + \varphi^2 \Phi^{(2)} + \dots$$

$$\tilde{V} = \varphi \tilde{V}^{(1)} + \varphi^2 \tilde{V}^{(2)} + \dots$$

$$\rho = \rho^{(0)} + \varphi \rho^{(1)} + \varphi^2 \rho^{(2)} + \dots$$

$\varphi = 0$: equilibrium / Poisson-Boltzmann
solution in the absence
of driving

$$\vec{\nabla} \cdot \vec{v}^{(1)} = 0$$

$$0 = -\vec{\nabla} p^{(1)} + \eta \vec{\nabla}^2 \vec{v}^{(1)} - \sum_a z_a e c_a^{(1)} \vec{\nabla} \phi^{(0)} - \sum_a z_a e c_a^{(0)} \vec{\nabla} \phi^{(1)}$$

$$\vec{\nabla} \cdot \left\{ -\vec{\nabla} c_a^{(1)} - \frac{z_a e}{k_B T} \left[c_a^{(1)} \vec{\nabla} \phi^{(0)} + c_a^{(0)} \vec{\nabla} \phi^{(1)} \right] \right\} = 0$$

$$\sum \vec{\nabla}^2 \phi^{(1)} + \sum_a z_a e c_a^{(1)} = 0$$

look at the equations far away from the

Debye layer ; $\vec{\nabla} p^{(1)} = 0$, $\vec{\nabla} \phi^{(0)} = 0$, $\sum_a z_a e c_a^{(0)} = 0$
 $c_a^{(1)} = 0$

$$\vec{\nabla} \cdot \left(c_a^{(0)} \vec{\nabla} \phi^{(1)} \right)$$

$$= \underbrace{\vec{\nabla} c_a^{(0)}}_{=0} \cdot \vec{\nabla} \phi^{(1)} + c_a^{(0)} \underbrace{\vec{\nabla}^2 \phi^{(1)}}_{\propto \underbrace{\sum_a z_a e c_a^{(1)}}_{=0}} = 0$$

→ away from the Debye layer:

$$\left\{ \begin{array}{l} \vec{\nabla} \cdot \vec{v}^{(1)} = 0 \\ \vec{\nabla}^2 \vec{v}^{(1)} = 0 \\ \vec{\nabla}^2 \phi^{(1)} = 0 \end{array} \right.$$

Ansatz: $\phi^{(1)} = - \vec{E}_{\text{ext}} \cdot \vec{r} + \psi \leftarrow \text{decays for } r \rightarrow \infty$

$$\vec{V}^{(1)} = \mu e \vec{E}_{\text{ext}} + \vec{\nabla} \Theta \leftarrow \text{decays for } r \rightarrow \infty$$

unknown
mobility

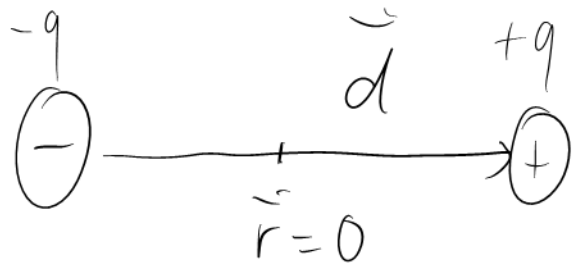
and

$$\vec{\nabla}^2 \Theta = 0$$

$$\vec{\nabla}^2 \psi = 0$$

assume dipolar symmetry for Θ and ψ

Excursion: Electrostatics of dipoles



def. " $\vec{d} q =: \vec{p}$ dipole moment

$$\Phi = -\frac{q}{4\pi\epsilon} \frac{1}{|\vec{r} + \vec{d}/2|} + \frac{q}{4\pi\epsilon} \frac{1}{|\vec{r} - \vec{d}/2|}$$

$$\frac{d}{r} \ll 1$$

$$\left(\vec{r} \pm \frac{\vec{d}}{2} \right)^2 = r^2 + \frac{d^2}{4} \pm \vec{r} \cdot \vec{d} = r^2 \left\{ 1 + \underbrace{\frac{d^2}{4r^2}}_{\text{neglect}} \pm \frac{\vec{r} \cdot \vec{d}}{r^2} \right\}$$

$$\approx r^2 \left[1 \pm \frac{\vec{r} \cdot \vec{d}}{r^2} \right]$$

$$\frac{1}{|\vec{r} \pm \vec{d}/2|} = \left[\left(\vec{r} \pm \frac{\vec{d}}{2} \right)^2 \right]^{-1/2} \approx \left[r^2 \left(1 \pm \frac{\vec{d} \cdot \vec{r}}{r^2} \right) \right]^{-1/2}$$

$$= \frac{1}{r} \left(1 \pm \frac{\vec{d} \cdot \vec{r}}{2r^2} \right) \approx \frac{1}{r} \pm \frac{\vec{r} \cdot \vec{d}}{2r^3}$$

$$\phi \approx \frac{q}{4\pi\epsilon} \left\{ -\frac{1}{r} + \frac{\vec{r} \cdot \vec{d}}{2r^3} + \frac{1}{r} + \frac{\vec{r} \cdot \vec{d}}{2r^3} \right\} = \frac{q}{4\pi\epsilon} \frac{\vec{r} \cdot \vec{d}}{r^3}$$

$r \gg d$

$$= \frac{\vec{p} \cdot \vec{r}}{4\pi\epsilon r^3}$$

solution of $\vec{\nabla}^2 \phi = 0$

end of excursion

ansatz $\varphi = \frac{\vec{p} \cdot \vec{r}}{4\pi \epsilon r^3}$ with unknown \vec{p}

resulting electric field? $-\vec{\nabla} \varphi = ?$

$$-\partial_\alpha \varphi = -\frac{1}{4\pi\epsilon} \partial_\alpha \left\{ p_\beta x_\beta (x_\delta x_\delta)^{-3/2} \right\} = \dots$$

$$-\vec{\nabla} \varphi = \frac{1}{4\pi\epsilon} \left\{ \frac{3}{r^5} (\vec{p} \cdot \vec{r}) \vec{r} - \frac{1}{r^3} \vec{p} \right\}$$

$$\boxed{\vec{E}^{(n)} = \vec{E}_{\text{ext}} + \frac{1}{4\pi\epsilon} \left\{ \frac{3}{r^5} (\vec{p} \cdot \vec{r}) \vec{r} - \frac{1}{r^3} \vec{p} \right\}}$$

$$\vec{v}^{(1)} = \mu e \vec{E}_{\text{ext}} + \frac{3}{r^5} (\vec{\Pi} \cdot \vec{r}) \vec{r} - \frac{1}{r^3} \vec{\Pi}$$

with unknown "velocity dipole moment" $\vec{\Pi}$

Debye layer is infinitely thin \rightarrow effect of the layer is encoded in the boundary conditions

$\vec{v}^{(1)}$: parallel to the surface at $|\vec{r}| = R$

$$\vec{v}^{(1)} \cdot \vec{r} = 0 \quad \text{at} \quad |\vec{r}| = R$$

$$0 = \mu_e \vec{E}_{ext} \cdot \vec{r} + \frac{3}{r^3} \vec{\pi} \cdot \vec{r} - \frac{1}{r^3} \vec{\pi} \cdot \vec{r}$$

$$|\vec{r}| = R$$

$$= \mu_e \vec{E}_{ext} \cdot \vec{r} + \frac{2}{r^3} \vec{\pi} \cdot \vec{r}$$

$$\Rightarrow \mu_e \vec{E}_{ext} + \frac{2}{R^3} \vec{\pi} = 0$$

$$\vec{\pi} = -\frac{1}{2} R^3 \mu_e \vec{E}_{ext}$$

$\vec{E}^{(n)}$ at the surface:

$\vec{E}^{(n)} \parallel \text{surface}$ (perfect screening)

$$0 = \vec{E}_{ext} \cdot \vec{r} + \frac{1}{4\pi\epsilon} \left\{ \frac{3}{r^3} (\vec{p} \cdot \vec{r}) - \frac{1}{r^3} (\vec{p} \cdot \vec{r}) \right\}$$

$$\uparrow$$
$$|\vec{r}| = R \quad = \vec{E}_{ext} \cdot \vec{r} + \frac{1}{4\pi\epsilon} \frac{2}{R^3} (\vec{p} \cdot \vec{r})$$

$$\vec{E}_{ext} + \frac{1}{2\pi\epsilon} \frac{1}{R^3} \vec{p} = 0 \quad \vec{p} = -2\pi\epsilon \vec{E}_{ext} R^3$$

velocity at surface; $\hat{r} = \vec{r} / |\vec{r}|$

$$\vec{V}^{(1)} = m_e \vec{E}_{ext} + \frac{3}{R^3} (\vec{\Pi} \cdot \hat{r}) \hat{r} - \frac{1}{R^3} \vec{\Pi} =$$

$$= m_e \vec{E}_{ext} + \frac{3}{R^3} \left(-\frac{1}{2} m_e R^3 \right) (\vec{E}_{ext} \cdot \hat{r}) \hat{r}$$

$$- \frac{1}{R^3} \left(-\frac{1}{2} m_e R^3 \right) \vec{E}_{ext} =$$

$$= m_e \vec{E}_{ext} \left\{ 1 - \frac{3}{2} \hat{r} \otimes \hat{r} + \frac{1}{2} \right\} =$$

$$= \frac{3}{2} m_e \vec{E}_{ext} (1 - \hat{r} \otimes \hat{r})$$

first-order field at surface

$$\vec{E}^{(1)} = \vec{E}_{\text{ext}} + \frac{1}{4\pi\epsilon} \left(\frac{3}{R^3} (\vec{p} \cdot \hat{r}) \hat{r} - \frac{1}{R^3} \vec{p} \right) =$$

$$= \vec{E}_{\text{ext}} + \frac{1}{2} \left\{ 3 \left(\frac{\vec{p}}{2\pi\epsilon R^3} \cdot \hat{r} \right) \hat{r} - \frac{\vec{p}}{2\pi\epsilon R^3} \right\} =$$

$$= \vec{E}_{\text{ext}} + \frac{1}{2} \left[3 (-\vec{E}_{\text{ext}} \cdot \hat{r}) \hat{r} + \vec{E}_{\text{ext}} \right] =$$

$$= \frac{3}{2} \vec{E}_{\text{ext}} \left[1 - \hat{r} \otimes \hat{r} \right]$$

$\vec{v}^{(1)} = \mu e \vec{E}^{(1)}$ at the surface, throughout

~ we can apply the picture of electro-osmosis

$$\mu = \frac{\epsilon \zeta}{e \eta}$$

M. von Smoludowski

1903

Gel electrophoresis → electrophoresis

motion of the sphere driven by field

μ : electrophoretic mobility