TMT4252 Electrochemistry: Poisson's & Laplace's equations

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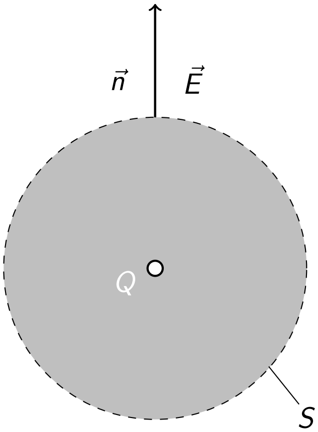
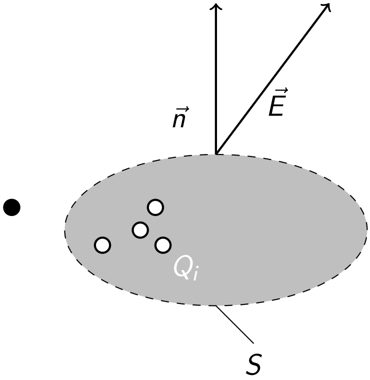
Surface integral over a closed, spherical surface enclosing a point charge Q:



$$\Phi = \iint_S \vec{E} \cdot \vec{n} dS = X(R) \iint_S dS = \frac{Q}{4\pi\epsilon R^2} 4\pi R^2 = \frac{Q}{\epsilon} \quad (1)$$

Gauss' law for the electric field



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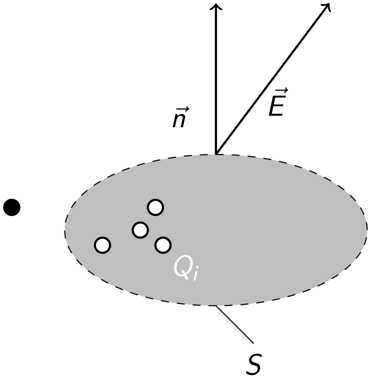

- The surface S is arbitrary
- Only charges inside S contribute to the flux

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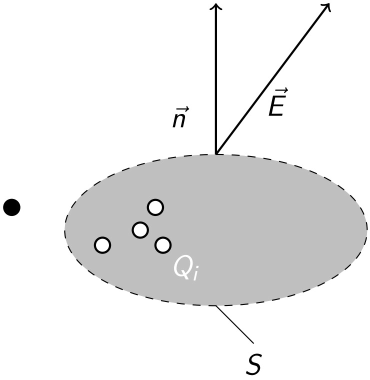

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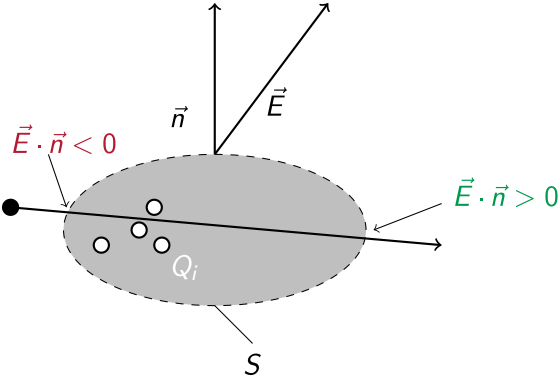
- Only charges inside S contribute to the flux

$$\boxed{\Phi = \iint_S \vec{E} \cdot \vec{n} dS = \frac{Q_1 + Q_2 + Q_3 + \ldots}{\epsilon}} \qquad (2)$$

The point outside contributes twice to the flux — but with opposite signs, and the net is zero



Some useful theorems . . .

Divergence theorem:

$$\iiint_V \vec{\nabla} \cdot \vec{F} dV = \iint_S \vec{F} \cdot \vec{n} dS \tag{3}$$

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A point in V, (x_0, y_0, z_0) exists (*mean value theorem*) so that

$$\iiint_V f(x, y, z)\, dV = V f(x_0, y_0, z_0) \tag{5}$$

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Divide by volume

Let $f = \vec{\nabla} \cdot \vec{F} = \vec{\nabla} \cdot \vec{E}$:

$$\frac{1}{V} \iiint\limits_V \vec{\nabla} \cdot \vec{E} dV \overset{Eq.\ (5)}{=} \vec{\nabla} \cdot \vec{E}\,(x_0, y_0, z_0) \tag{6}$$

$$\frac{1}{V} \iiint\limits_V \vec{\nabla} \cdot \vec{E} dV \overset{Eq.\ (4)}{=} \frac{1}{V} \iint\limits_S \vec{E} \cdot \vec{n} dS \tag{7}$$

$$\overset{\text{Gauss}}{=} \frac{1}{V} \sum_i \frac{Q_i}{\epsilon} \tag{8}$$

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. . . and in the limit $V \to 0$

Limit:

$$\vec{\nabla} \cdot \vec{E}\,(x_0, y_0, z_0) = \lim_{V \to 0} \frac{1}{V} \sum_i \frac{Q_i}{\epsilon} \tag{9}$$

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or **Gauss's law on differential form**:

$$\vec{\nabla} \cdot \vec{E}\,(x, y, z) = \frac{\rho\,(x, y, z)}{\epsilon} \tag{10}$$

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where

$$\boxed{\rho = \lim_{V \to 0} \frac{1}{V} \sum_i Q_i} \tag{11}$$

is the **charge density**: $[\rho] = \mathrm{C\,m^{-3}}$.

Poisson's & Laplace's equations

$\vec{E} \overset{\text{déf}}{=} -\vec{\nabla}\phi$ gives **Poisson's equation**:

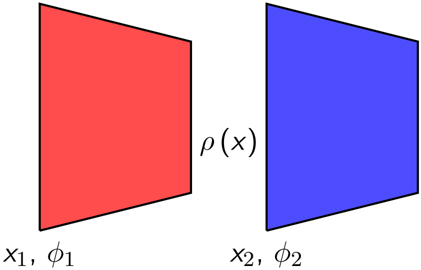
$$\boxed{\nabla^2\phi(x,y,z) = -\frac{\rho(x,y,z)}{\epsilon}} \qquad (12)$$

Bulk (electroneutrality), $\rho = 0$, **Laplace's equation**:

$$\boxed{\nabla^2\phi(x,y,z) = 0} \qquad (13)$$

$\rho \neq 0$: **space charge regions** (pn-juntions, electrochemical interfaces, membranes, . . .)

Example: The potential distribution between two parallel plates and constant $\rho(x) = \rho$



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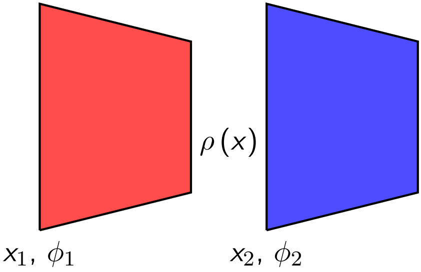

The Poisson equation in one dimension:

$$\frac{d^2\phi}{dx^2} = -\frac{\rho(x)}{\epsilon} \tag{14}$$

Example: Poisson equation in one dimension and constant $\rho(x) = \rho$

We integrate the Poisson equation once from x_1 to x

$$\int_{x_1}^{x} \frac{d^2\phi}{dx^2} dx = -\frac{1}{\epsilon} \int_{x_1}^{x} \rho dx \tag{15}$$

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The electric field between the planes is therefore

$$X = X_1 + \frac{\rho}{\epsilon}(x - x_1) \quad (19)$$

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$$\phi = \phi_1 - X_1 (x - x_1) - \frac{\rho}{2\epsilon}(x - x_1)^2 \quad (20)$$

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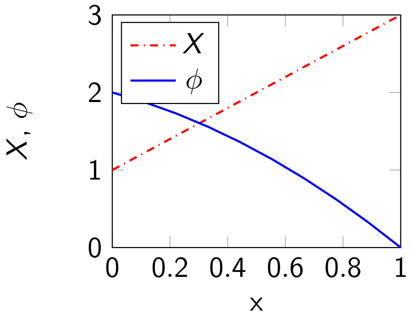

Figure: Potential and electric field for two parallel plates enclosing a constant charge density ρ.