Dynamics of Gels part 4

Masao Doi
Tokyo University

Outline

1.What are gels: problems to be discussed

2.Basic equations for gel dynamics:linear model

3Applications:

Swelling of constrained gel

Swelling of cylindrical gel

4.Basic equations for gel dynamics: non-linear model

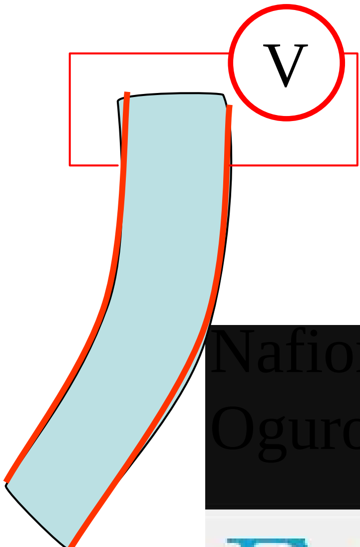
Theory of elasticity for large deformation

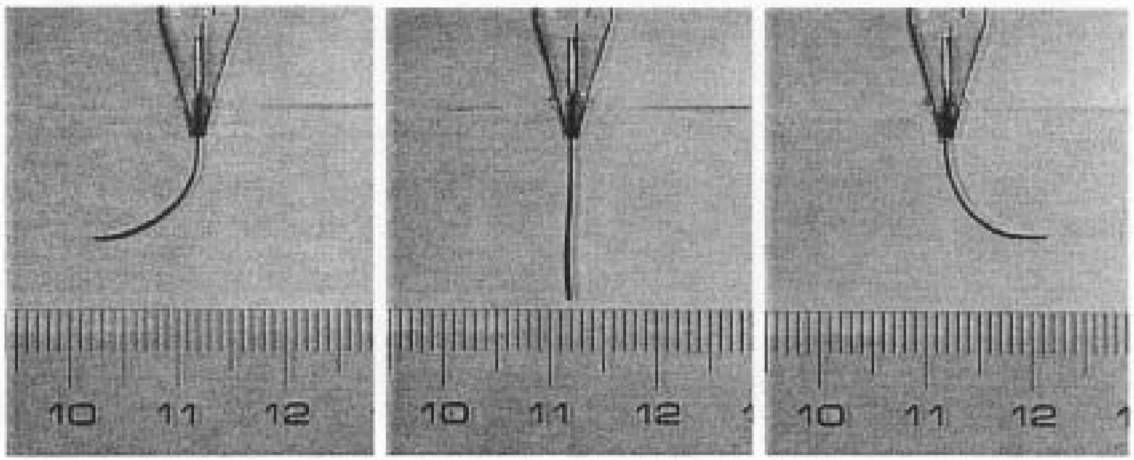
Volume transition

5.Electro-kinetic effect

Electro Responsive Gel

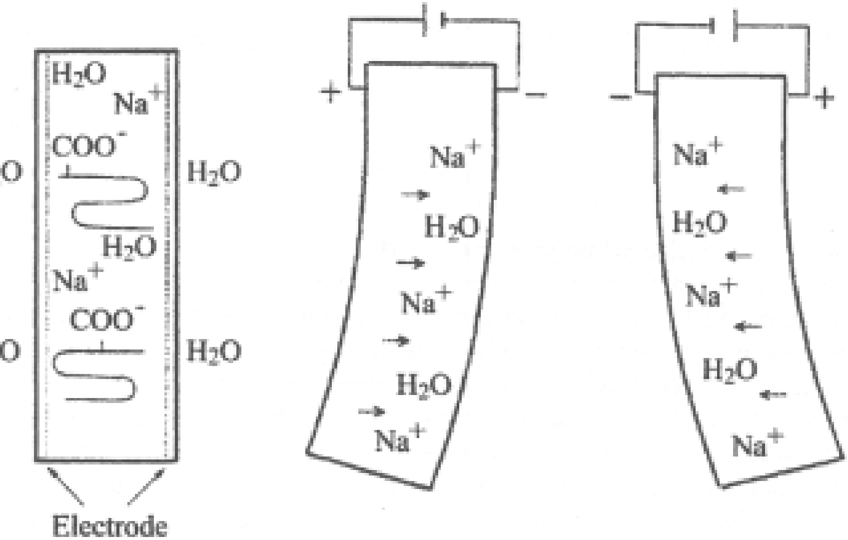
Electric field causes deformation of ionic gels.





Nafion
Oguro et al

Mechanism



Asaka et al (1995, 2000)

Water is carried by mobile ions.

de Gennes et al (2000)

Electro Mechanical Coupling

Electric current

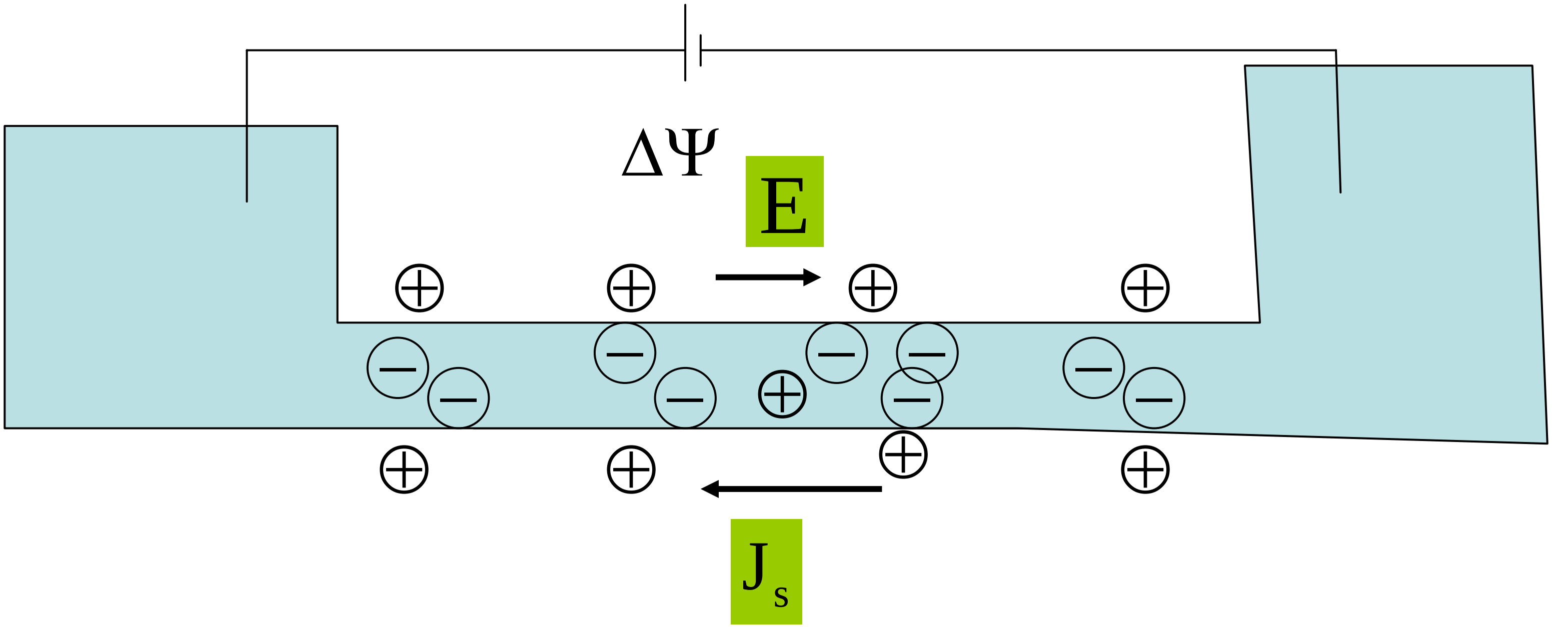
$$J = -\sigma \nabla \psi - \lambda \nabla p$$

Water flux

$$J_s = -\kappa \nabla p - \lambda \nabla \psi$$

Electro-Osmosis

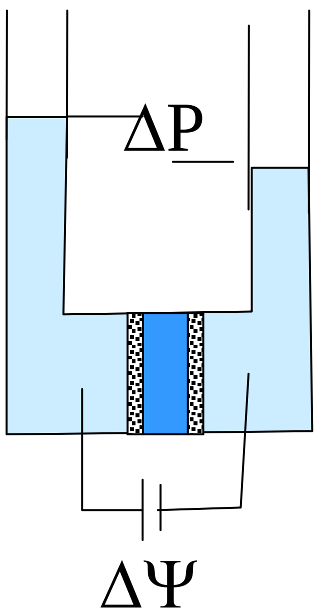
$$J_s = -\kappa \nabla p - \lambda \nabla \psi$$



Electro-mechanical coupling

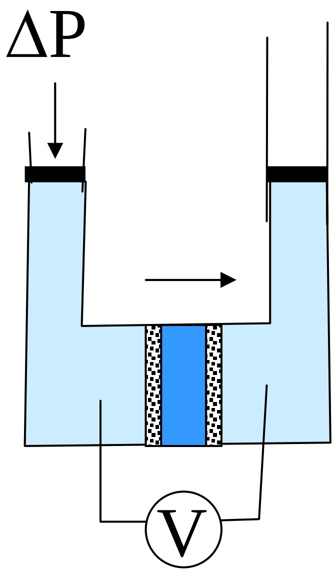
$$J = -\sigma \nabla \psi - \lambda \nabla p$$

$$J_s = -\kappa \nabla p - \lambda \nabla \psi$$



Electro osmosis

$$\Delta P = -\frac{\lambda}{\kappa} \Delta \Psi$$



Streaming potential

$$\Delta \Psi = -\frac{\lambda}{\sigma} \Delta P$$

Basic Equations for Ionic Gels

$$\nabla \bullet (\sigma - p\mathbf{I}) = 0$$

mechanical balance

$$\mathbf{J}_s = -\kappa \nabla \bullet p - \lambda \nabla \psi$$

water flow

$$\nabla \bullet [\phi \mathbf{v}_p + (1 - \phi)\mathbf{v}_s] = 0$$

incompressible

$$\mathbf{J} = -\sigma \nabla \bullet \psi - \lambda \nabla p$$

electric current

$$\nabla \bullet \mathbf{J} = 0$$

charge neutrality

"Derivation" of Basic Equations

$$\zeta_i(\mathbf{v}_i - \mathbf{v}_s) = -q_i \nabla \psi$$ ions

$$\zeta_p c_p(\dot{\mathbf{u}} - \mathbf{v}_s) = \nabla \bullet \sigma - \phi \nabla p - c_p q_p \nabla \psi$$ polymer

$$\zeta_p c_p(\mathbf{v}_s - \dot{\mathbf{u}}) + \zeta_i c_i(\mathbf{v}_s - \mathbf{v}_i) = (1-\phi)\nabla p$$ water

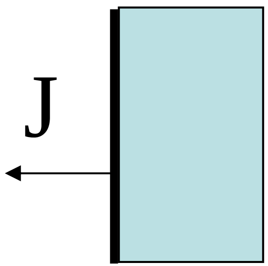
$$\mathbf{J}_s = (1-\phi)\left(\mathbf{v}_s - \dot{\mathbf{u}}\right)$$ water flux

$$\mathbf{J} = \sum_i c_i q_i (\mathbf{v}_i - \dot{\mathbf{u}})$$ electric current

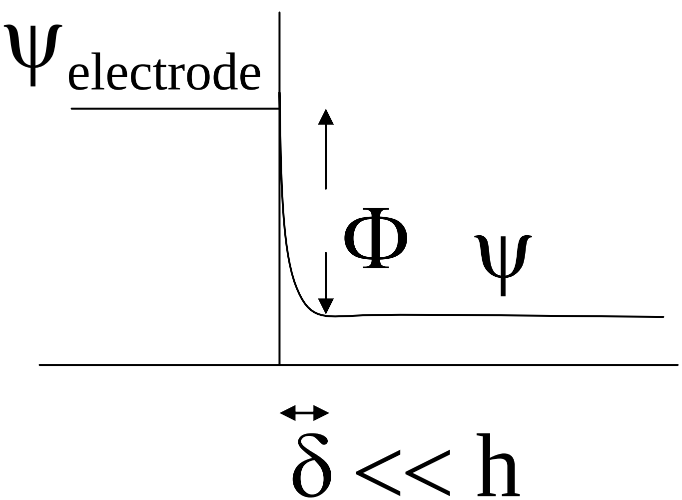
$$\kappa = \frac{(1-\phi)^2}{c_p \zeta_p} \qquad \sigma = \frac{c_p q_p^2}{\zeta_p} + \sum_i \frac{c_i q_i^2}{\zeta_i} \qquad \lambda = \frac{q_p(1-\phi)}{\zeta_p}$$

Boundary Condition 1

Condition for electric field and current



$$\mathbf{J} \bullet \mathbf{n} = \begin{cases} \dot{Q} & \Phi < \Phi_c \\ J_{electrode}(\Phi) & \Phi > \Phi_c \end{cases}$$

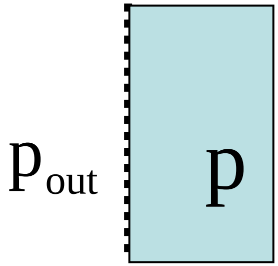


$$\psi = \psi_{electrode} - \Phi(Q)$$

Boundary Condition 2

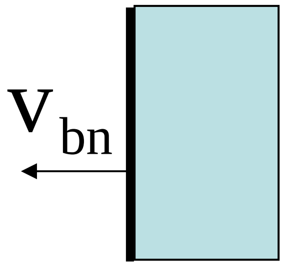
Condition for solvent

permeable wall



$$p = p_{out}$$

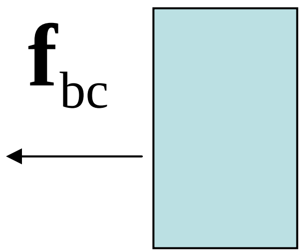
Impermeable wall



$$v_{sn} = v_{bn}$$

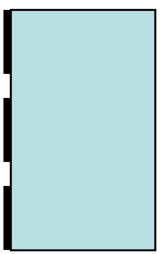
Condition for polymer

deformable boundary



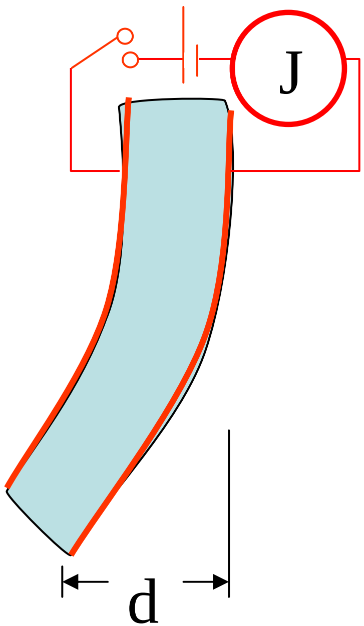
$$(\sigma - pI) \bullet \mathbf{n} = \mathbf{f}_{bc}$$

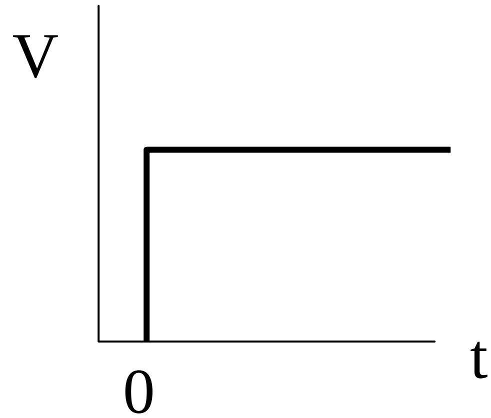
gel fixed to the boundary

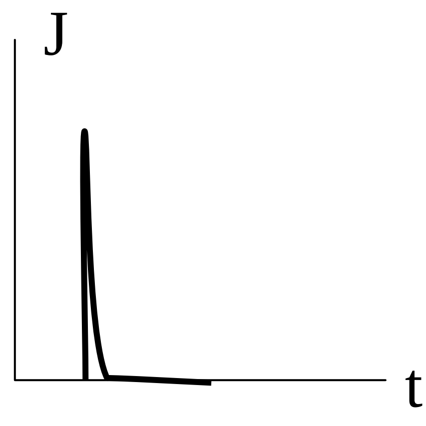


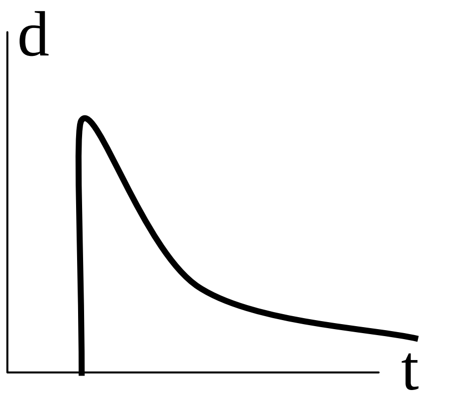
$$\mathbf{u}_p = \mathbf{u}_b$$

Analysis of the Step Voltage Case

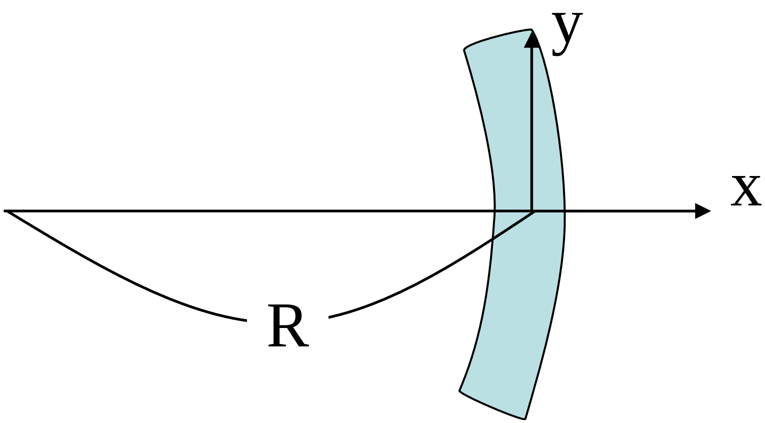








Mechanical Balance



$$u_x(x,t)$$

$$u_y = \frac{xy}{R}, u_z = \frac{xz}{R}$$

$\sigma_{xx}, \sigma_{yy}, \sigma_{zz}$ are written by

$\beta(x,t) = \nabla \bullet \mathbf{u}$ and $R(t)$.

$$\sigma_{xx} = (K + \frac{4}{3}G)\beta - \frac{4G}{R}x$$

$$\sigma_{yy} = (K - \frac{2}{3}G)\beta + \frac{2G}{R}x$$

Force balance in x direction

$$P = \sigma_{xx}$$

Torque balance

$$\int_{-h}^{h} dx(\sigma_{yy} - P)x = 0$$

$$\frac{1}{R(t)} = \frac{1}{h^3}\int_0^h dx\beta(x,t)x$$

Initial Condition

Assume that the charging up of the electric double layer is very fast.

For $t < \tau_s$

$$\mathbf{J} = -\sigma \nabla \bullet \psi$$

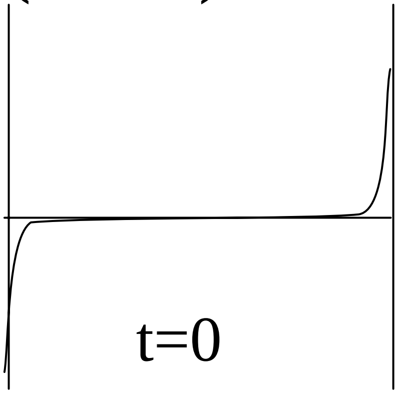
$$\nabla p = 0 \qquad \mathbf{J}_s = -\lambda \nabla \psi$$

Total amount of water transferred

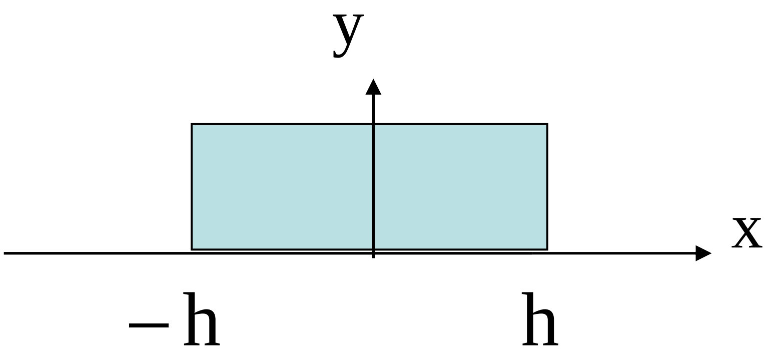
$$w = \frac{\lambda}{\sigma} Q$$

$$\beta(x, t=0) = -w\delta(x+h) + w\delta(x-h)$$

$$\frac{1}{R(0)} = \frac{2\lambda}{h^2 \sigma} Q$$



Relaxation



$$J = -\sigma\nabla\psi - \lambda\nabla p$$

$$J_s = -\kappa\nabla p - \lambda\nabla\psi$$

$$J = 0$$

$$J_s = -\left(\kappa - \frac{\lambda^2}{\sigma}\right)\frac{\partial p}{\partial x}$$

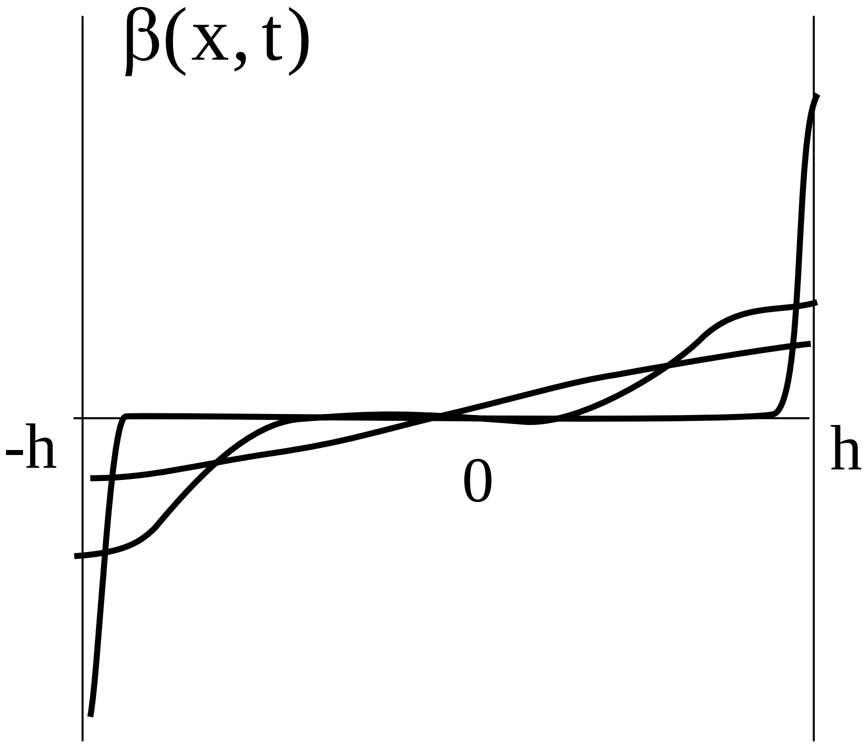
$$\frac{\partial\beta}{\partial t} = D'\frac{\partial^2\beta}{\partial x^2}$$

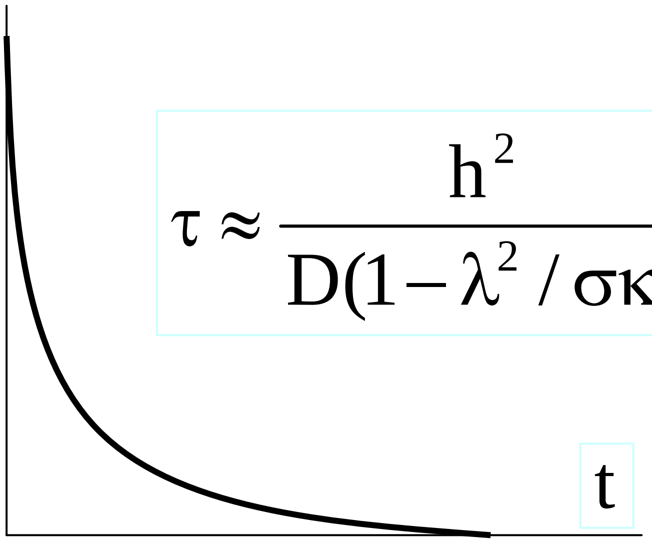
$$D' = \kappa\left(1 - \frac{\lambda^2}{\kappa\sigma}\right)\left(K + \frac{4}{3}G\right)$$

$$\frac{\partial\beta}{\partial x} = \frac{4G}{K+(4/3)G}\frac{1}{R}$$

$$\frac{1}{R(t)} = \frac{1}{h^3}\int_0^h dx\,\beta(x,t)\,x$$

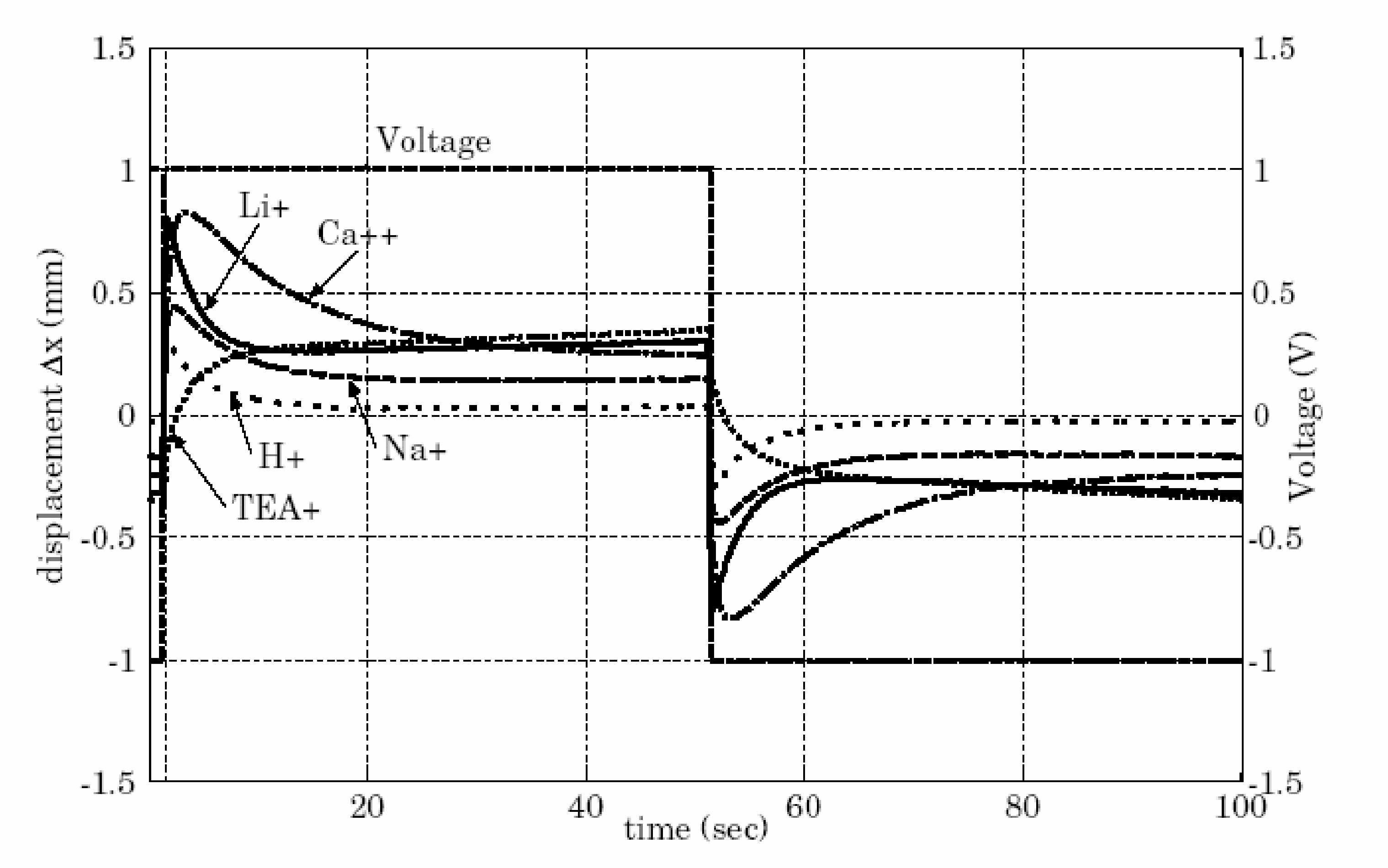
Time Evolution





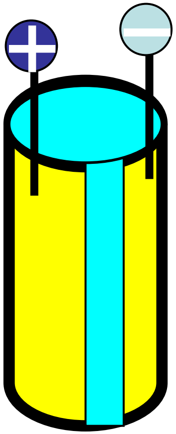
$$\tau \approx \frac{h^2}{D(1-\lambda^2/\sigma\kappa)}$$

Experimental results

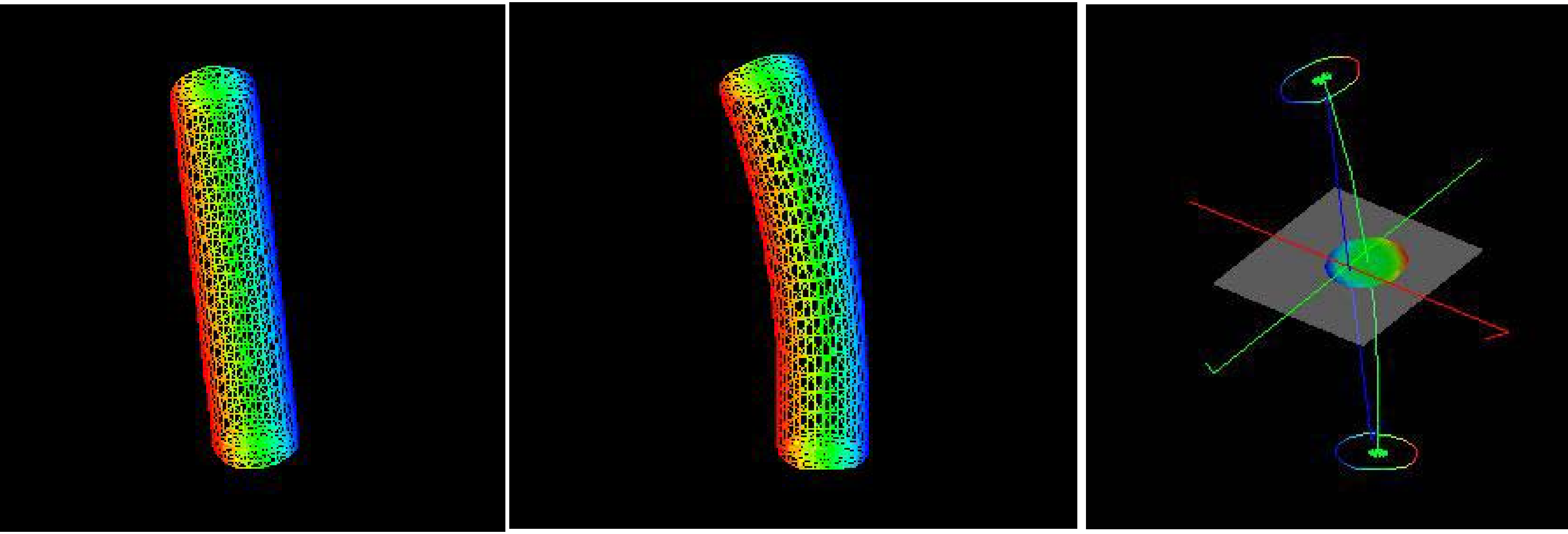


Gel does not become straight as $t \to \infty$

Deformation of Cylindrical Gel



Taniguchi and Yamaue



$\Delta\Psi$ *=0.3* **Ion distribution**

Conclusion

- The dynamics of ionic gel involves electro-stress-diffusion coupling
  - solvent diffusion
  - deformation of gel
  - electric field
- A complete set of equations for the phenomena has been established, but it has not been studied extensively.
- Application:
  - artificial muscle, biomechanics, fuel cell