

The development of Variational Methods for the investigation of Ion  
Transport in Hydrated Polymer Electrolyte Pores

**R. Paul**

NSERC

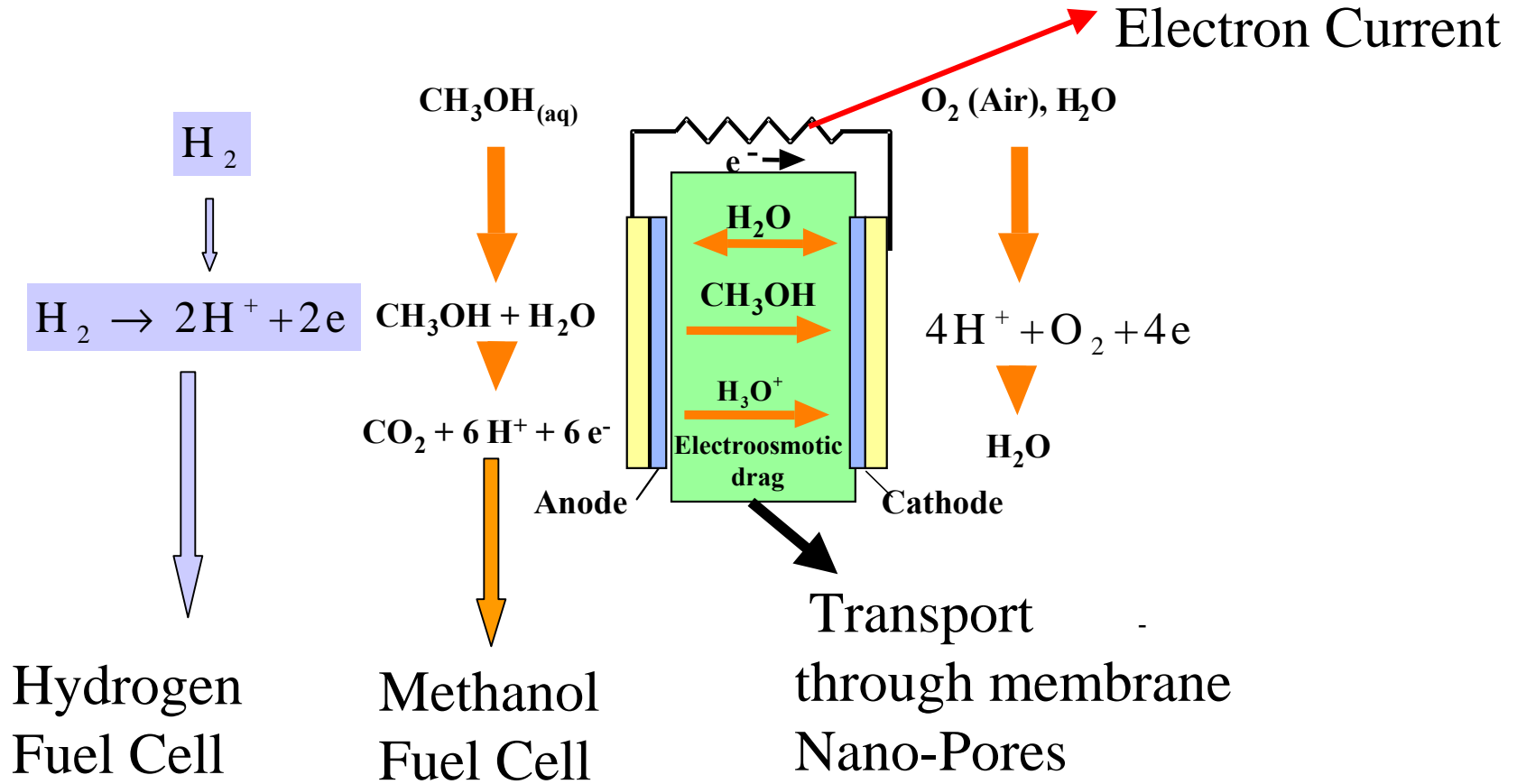
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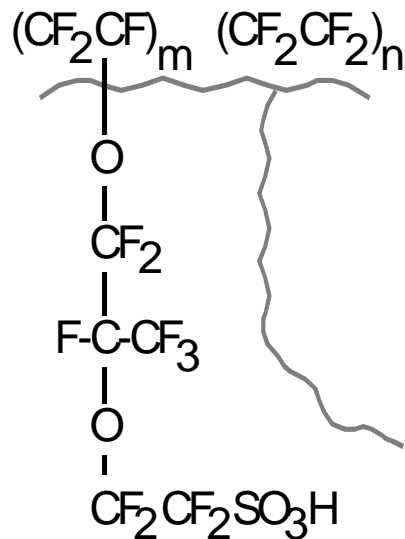
# A Polymer Electrolyte Membrane Fuel Cell Model :



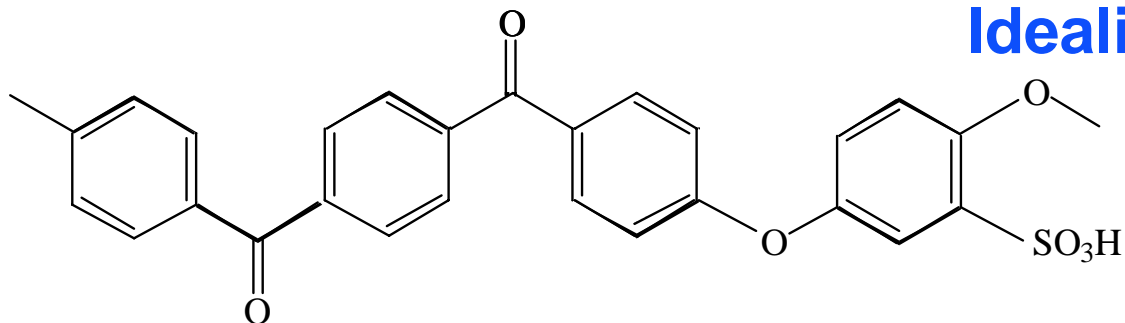
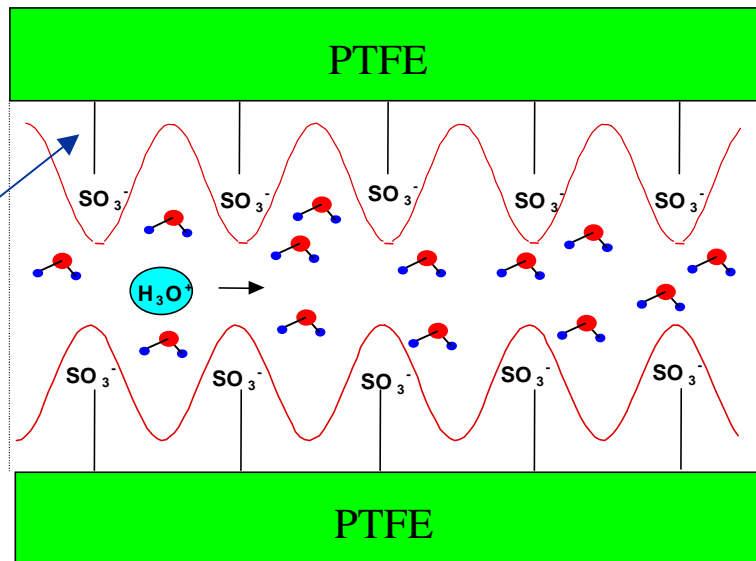
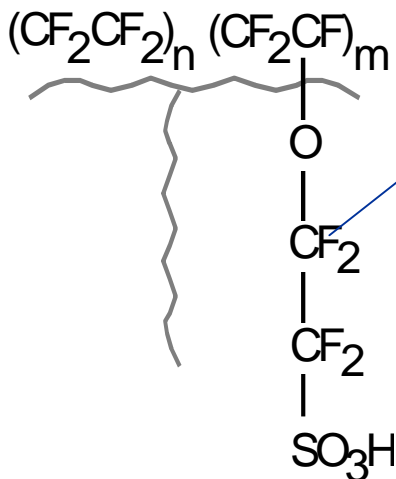
Electron Current through the external circuit depends upon the Protonic Current through the membrane.

# Perfluoro- and Aromatic Sulfonic Acid Membranes

Nafion 117 (EW=1100)



Dow Membrane  
(EW=800)

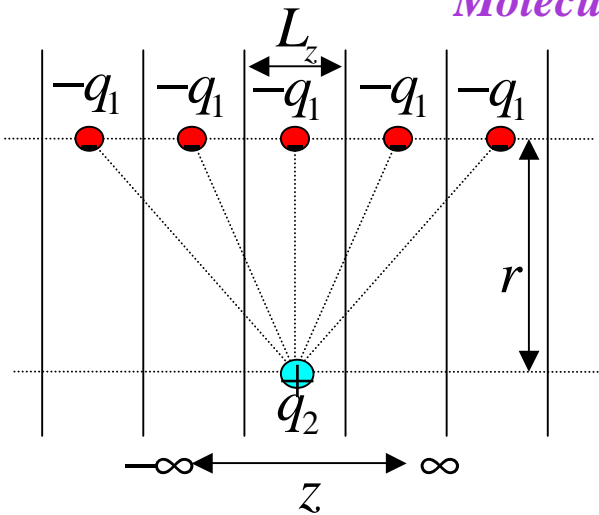


## Idealized Membrane Pore

PEEK (EW=700-900)

S.J. Paddison, R. Paul, and T.A. Zawodzinski, in *Proton Conducting Membrane Fuel Cells II*, S. Gottesfeld and T.F. Fuller, Editors, **PV 98-27**, 106-120, The Electrochemical Society Proceedings Series, Pennington, NJ (1999).

Groenbech-Jensen, N., Hummer, G., Beardmore, K. M., 1997, *Molecular Physics*, **92**, 941-945.

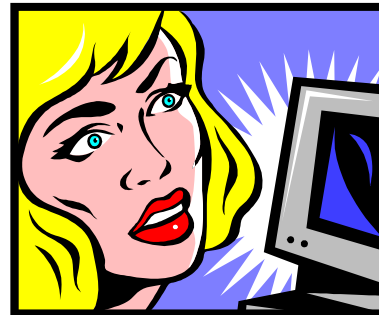


$$V_{12} = -\frac{q_1 q_2}{\pi \epsilon L_z} \sum_{n=1}^{\infty} K_0\left(\frac{2\pi n r}{L_z}\right) \cos\left(\frac{2\pi n z}{L_z}\right) + \frac{2q_1 q_2}{L_z} \ln\left(\frac{r}{r_0}\right)$$

- (1) S.J. Paddison, R. Paul, and T. Zawodzinski, *JECs*, **147**, 617, (2000)  
 (2) S.J. Paddison and R. Paul, *JCP*, **115**, 7753 (2001)

$$V_P = -\left| \frac{q_1 q_2}{\pi \epsilon L_z} K_0\left(\frac{2\pi r}{L_z}\right) \cos\left(\frac{2\pi z}{L_z}\right) \right|$$

Pore of infinite length??



# Non-equilibrium Statistical Mechanical Results compared with Experiment ( Data Provided by S. J. Paddison)

Experiments

Nafion® with  $\lambda = 6$ :  $D_\alpha = 5.05 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \Rightarrow 2.0 \times 10^{-10} < D_\alpha < 6.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$

$\lambda = 13$ :  $D_\alpha = 8.36 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \Rightarrow 7.0 \times 10^{-10} < D_\alpha < 1.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$

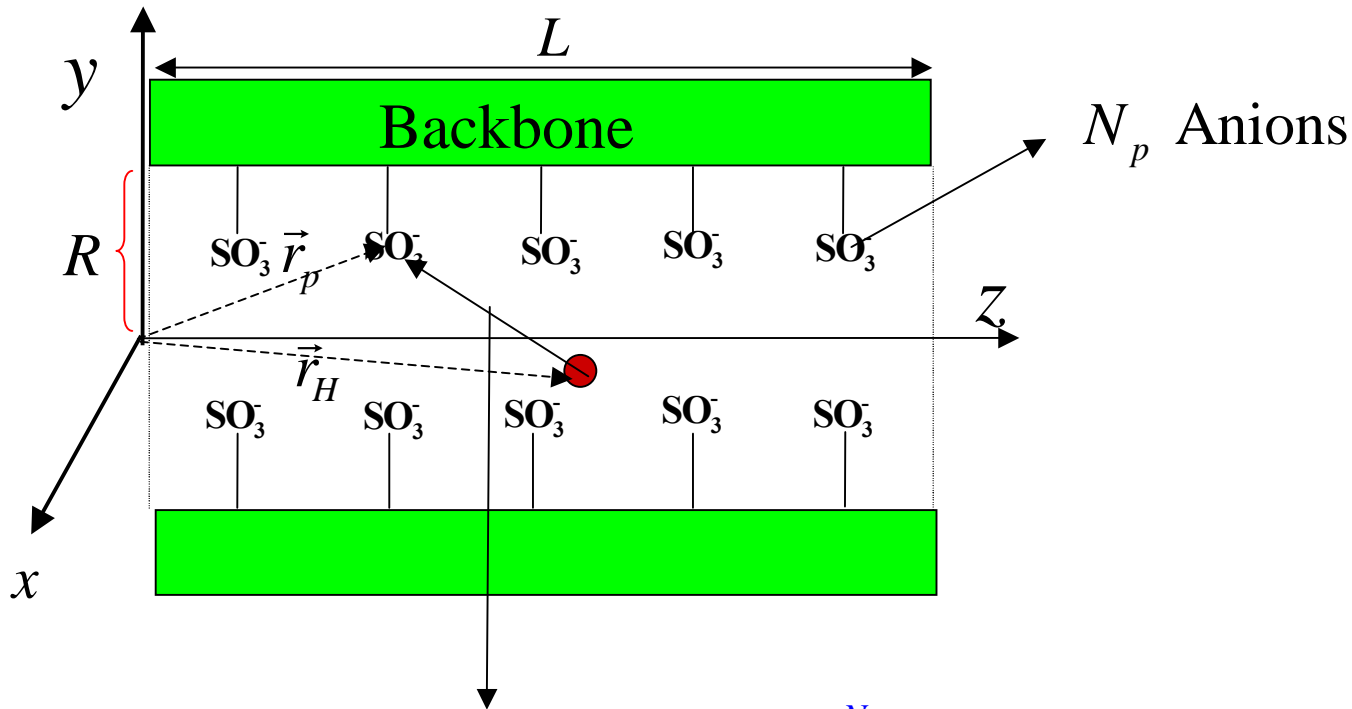
$\lambda = 22.5$ :  $D_\alpha = 1.92 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \Rightarrow 2.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$

PEEKK with  $\lambda = 15$ :  $D_\alpha = 4.13 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \Rightarrow 4.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$

$\lambda = 23$ :  $D_\alpha = 1.23 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \Rightarrow 1.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$

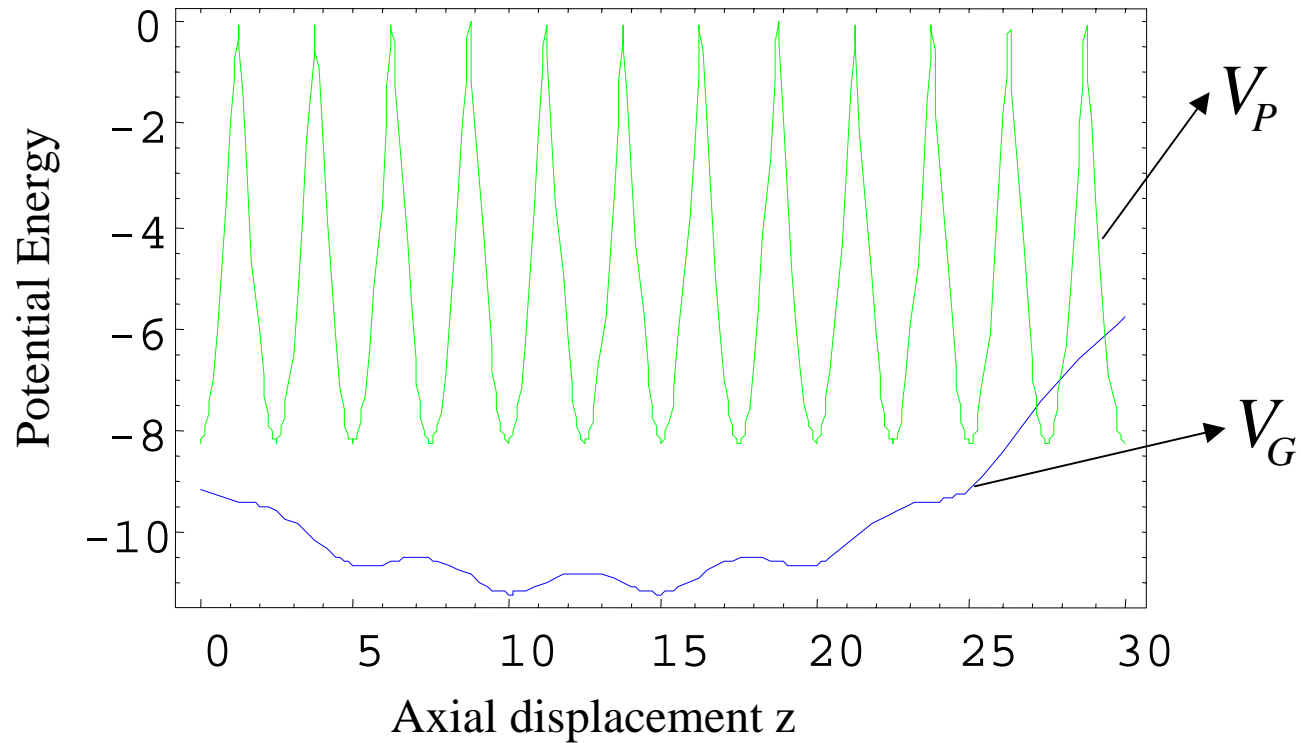
$\lambda = 30$ :  $D_\alpha = 1.54 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \Rightarrow 1.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$

Andrew Gillespie added the Coulombic potentials between all the anions in a pore and single hydronium ion → **Exact**



$$V_G(\vec{r}_H) = -\frac{e^2}{4\pi\epsilon} \sum_{p=1}^{N_p} \frac{1}{|\vec{r}_p - \vec{r}_H|}$$

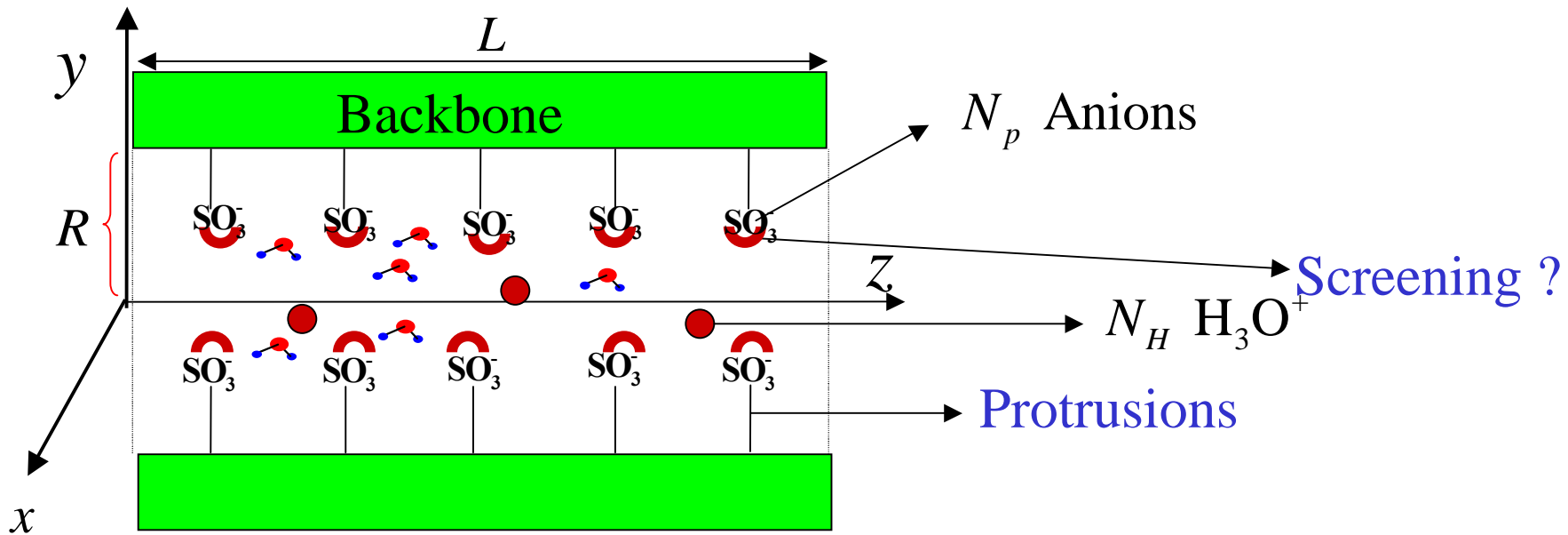
Comparing:



Friction coefficient will rise and diffusion coefficient will fall.

Charge screening suggested

# Model



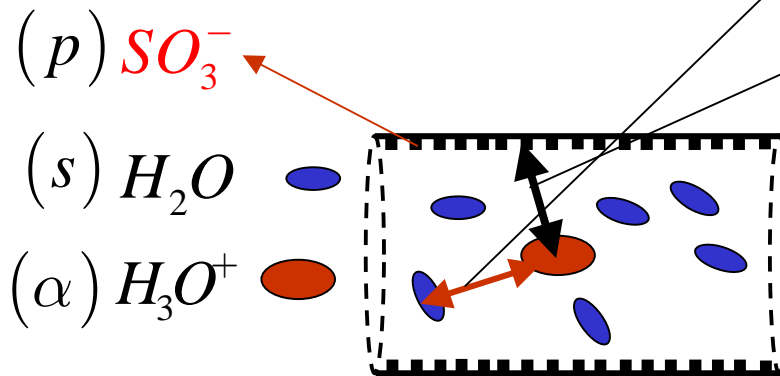
$\text{H}_3\text{O}^+$  : Shorthand:  $\alpha$

Of primary importance is the friction coefficient

$\zeta_\alpha =$  Friction Coefficient of ion  $\alpha$

Requires knowledge of electrostatic forces.

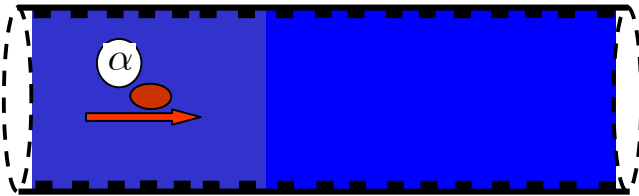
$$\vec{F}_\alpha^{\text{Mol.}}(\vec{r}_\alpha, \{\vec{r}\}_{\text{water}}) = \vec{F}_{\alpha s}^{\text{Mol.}}(\vec{r}_\alpha, \{\vec{r}\}_{\text{water}}) + \vec{F}_{\alpha p}^{\text{Mol.}}(\vec{r}_\alpha)$$



Average force:

$$\left\langle \vec{F}_\alpha(\vec{r}_\alpha, \vec{v}_\alpha) \right\rangle =$$

$$\int d\{\vec{r}\}_{\text{water}} d\{\vec{p}\}_{\text{water}} \vec{F}_\alpha^{\text{Mol}}(\vec{r}_\alpha, \{\vec{r}\}_{\text{water}}) f_{\text{Non-Eq.}}(\{\vec{r}\}_{\text{water}}, \{\vec{p}\}_{\text{water}}, \vec{r}_\alpha, \vec{v}_\alpha)$$



Non-Equilibrium distribution of Water molecules because of the Hydronium ion motion.

$$\left\langle \vec{F}_\alpha(\vec{r}_\alpha, \vec{v}_\alpha) \right\rangle \approx -\zeta_\alpha(\vec{r}_\alpha) \vec{v}_\alpha$$

$$\frac{kT}{\zeta_\alpha} = D_\alpha$$

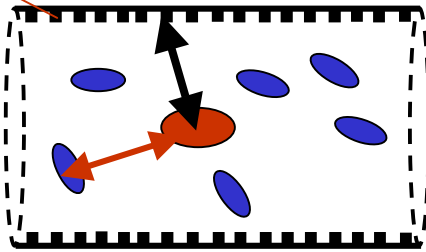
Desired Friction Coefficient

$$\vec{F}_\alpha^{\text{Mol.}}(\vec{r}_\alpha, \{\vec{r}\}_{\text{water}}) = \vec{F}_{\alpha s}^{\text{Mol.}}(\vec{r}_\alpha, \{\vec{r}\}_{\text{water}}) + \vec{F}_{\alpha p}^{\text{Mol.}}(\vec{r}_\alpha)$$

(p)  $SO_3^-$

(s)  $H_2O$

( $\alpha$ )  $H_3O^+$



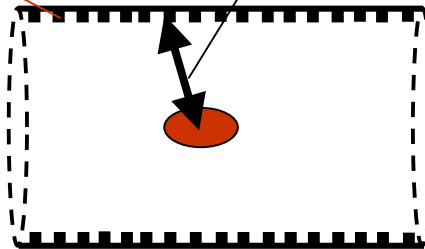
Primitive model  
used:  $H_2O$  treated  
as bulk continuum.



(p)  $SO_3^-$

$\vec{F}_{\alpha p}^{\text{Mol.}}(\vec{r}_\alpha)$

( $\alpha$ )  $H_3O^+$



**What is  
the potential  
behind this  
force ?**

In "bulk" electrochemistry use is made of the screened potential:

$$w_2^{\text{Coulombic}}(r) = \frac{e^2}{4\pi\epsilon r} \rightarrow w_2^{\text{Debye-Huckel}}(r) = \frac{e^2 e^{-\kappa r}}{4\pi\epsilon r}$$

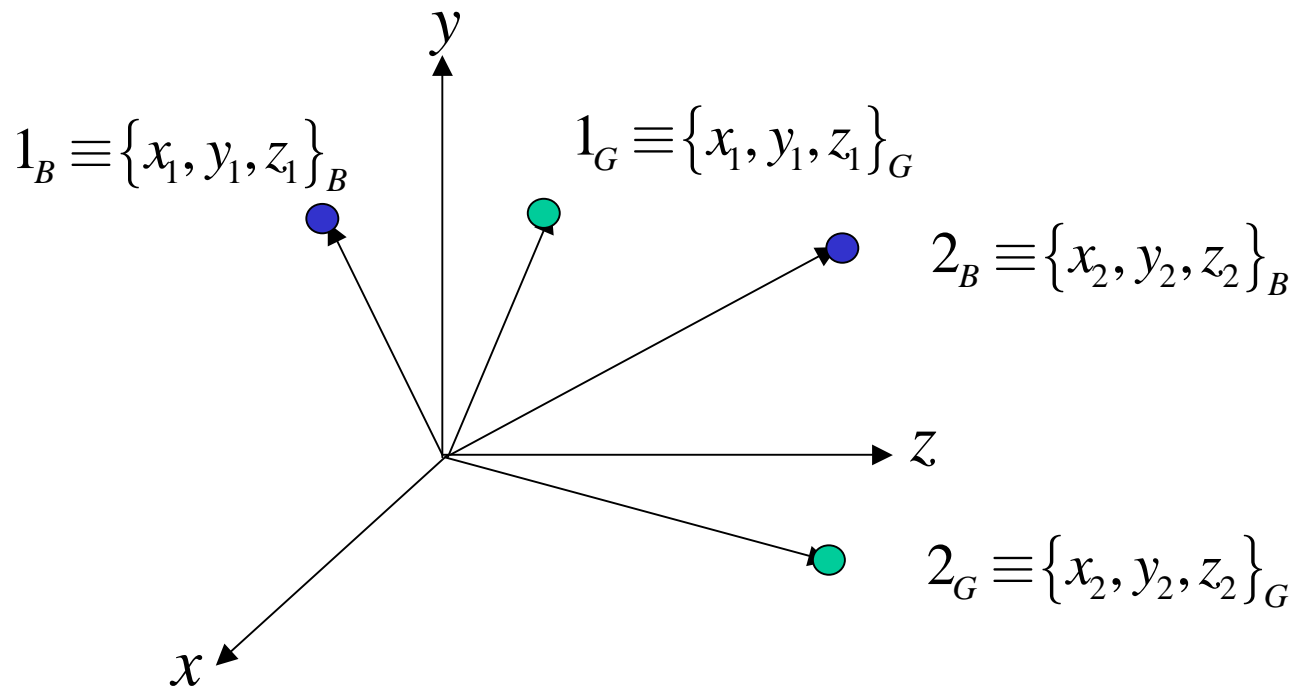
Derived by using Poisson-Boltzmann equation with several assumptions that do not hold in a nanopore environment.

**Can we do  
better?**

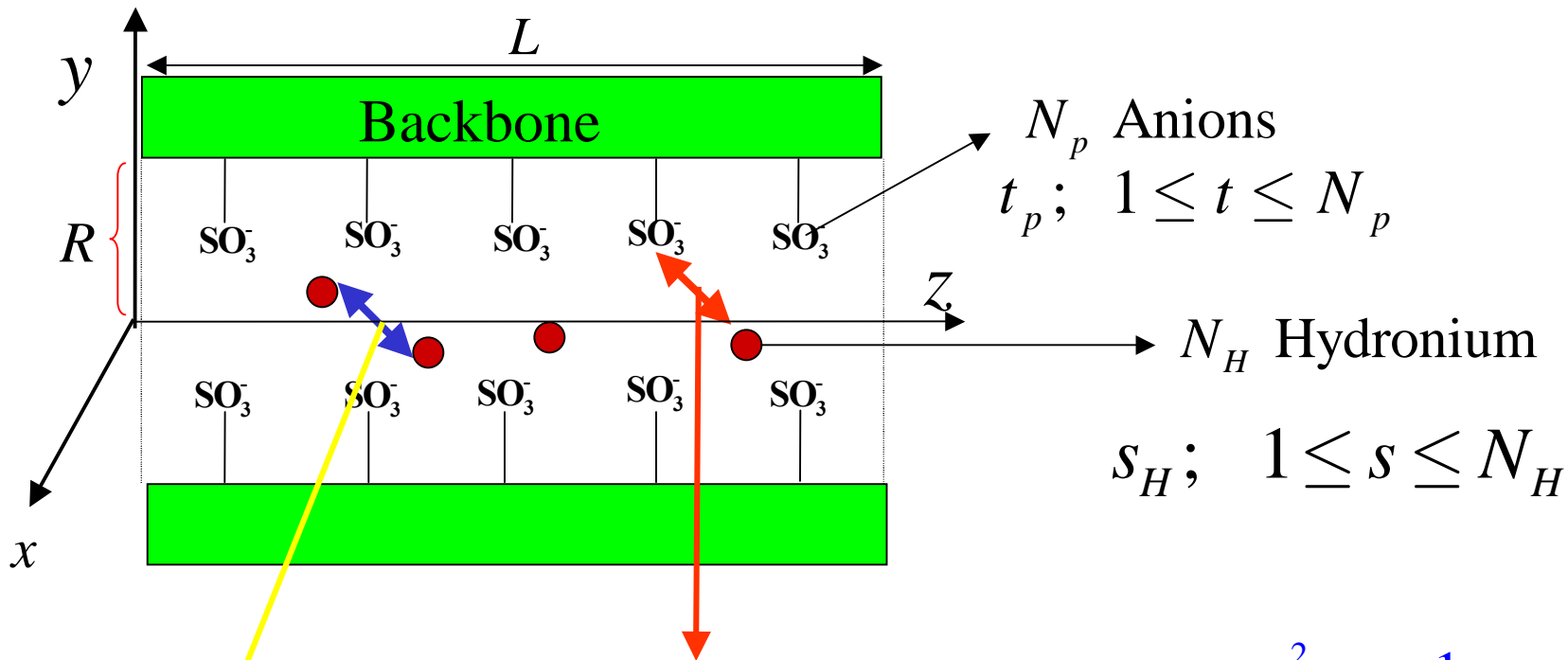
Resort to a statistical mechanical model.

Need a complete description of Hamiltonian, particularly the interaction energies.

# Coordinates for multicomponent systems



# Some interactions (Ignoring Charge Screening):



Potential: 1 anion & 1 hydronium:  $\psi_{pH}(t, s) = -\frac{e^2}{4\pi\epsilon} \frac{1}{|t_p - s_H|}$

Potential: hydronium/hydronium:  $\psi_{HH}(i, s) = \frac{e^2}{4\pi\epsilon} \frac{1}{|i_H - s_H|}$

# Total Potential

$$W_{\{p\},\{H\}} \left( \{1, 2, \dots, N_p\}, \{1, 2, \dots, N_H\} \right) =$$
$$\text{SO}_3^- / \text{H}_3\text{O}^+ \quad \text{H}_3\text{O}^+ / \text{H}_3\text{O}^+$$
$$\sum_{i=1}^{N_p} \sum_{j=1}^{N_H} \psi_{pH}(i, j) + \sum_{i=1}^{N_H} \sum_{j<i}^{N_H} \psi_{HH}(i, j)$$

Defining:

$$\beta = \frac{1}{kT}$$

N-Body distribution function:

$$n_{\{p\}\{H\}} \left( \{1, 2, \dots, N_p\}, \{1, 2, \dots, N_H\} \right) = \frac{1}{Z} e^{-\beta W_{\{p\}\{H\}} \left( \{1, 2, \dots, N_p\}, \{1, 2, \dots, N_H\} \right)}$$

$$Z = \int \prod_{i=1}^{N_p} di \prod_{j=1}^{N_H} dje^{-\beta W_{\{p\}\{H\}} \left( \{1, 2, \dots, N_p\}, \{1, 2, \dots, N_H\} \right)}$$

Reduced distribution functions:

2-body:

$$n_{pH}(1, 2) = N_p N_H \int \prod_{i=2}^{N_p} di \prod_{j=1, \neq 2}^{N_H} dj n_{\{p\}\{H\}} \left( \{1, 2 \dots N_p\}, \{1, 2 \dots N_H\} \right)$$

1-body

$$n_H(2) = N_H \int \prod_{i=1}^{N_p} di \prod_{j=1, \neq 2}^{N_H} dj n_{\{p\}\{H\}} \left( \{1, 2 \dots N_p\}, \{1, 2 \dots N_H\} \right)$$

$$n_{pH}(1,2) = n_p(1)n_H(2) \times \underbrace{e^{-\beta\Psi_{pH}(1,2)}}_{\text{Shorthand: } g_{pH}(1,2)}$$

Shorthand:  $g_{pH}(1,2)$

$\Psi_{pH}(1,2)$  **Average Potential** between  $p$  and  $H$  in presence of all other particles **integrated over**  $\rightarrow$  Desired quantity.

Total Correlation Function  $h_{pH}$ :  $h_{pH}(1,2) = e^{-\beta\Psi_{pH}(1,2)} - 1$

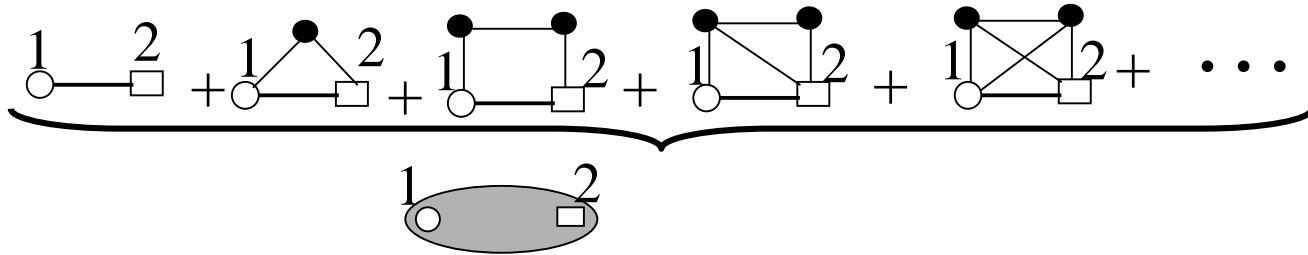
In addition:  $h_{pp}(i,j)$  &  $h_{HH}(i,j)$

Pictorial depiction of  $h_{pH}(1,2) = e^{-\beta\Psi_{pH}} - 1$

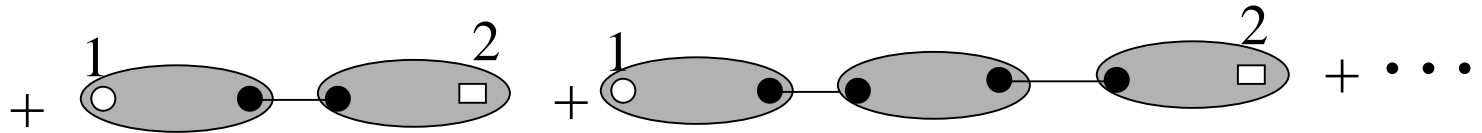
$\circ_1$  = Anion with coordinate 1       $\square_2$  Hydronium with coordinate 2

— = Bond       $\bullet$  = anion or hydronium whose coordinates are integrated over

$h_{pH}(1,2) =$



$c_{pH}(1,2) =$  Direct Correlation Function



$$h_{pH}(1,2) = c_{pH}(1,2) + \sum_{\gamma=H,p} \int d3 h_{p\gamma}(1,3) n_{\gamma}(3) c_{\gamma H}(3,2)$$

Ornstein-Zernicke Equation

## Approximations :

$$(1) h_{pH}(1, 2) = c_{pH}(1, 2) + \sum_{\gamma=H,p} \int d3 h_{p\gamma}(1, 3) n_{\gamma}(3) c_{\gamma H}(3, 2)$$

$$\approx c_{pH}(1, 2) + \int d3 h_{pH}(1, 3) n_H(3) c_{HH}(3, 2)$$

(2) Constant hydronium ion density.

(3) Dependence on relative distances.

$$(4) c_{pH}(1, 2) = \begin{array}{c} \text{1} \text{---} \text{2} \\ \text{○} \text{---} \text{□} \end{array} + \begin{array}{c} \bullet \\ \text{1} \text{---} \text{2} \\ \text{○} \text{---} \text{□} \end{array} + \begin{array}{c} \bullet \text{---} \bullet \\ \text{1} \text{---} \text{2} \\ \text{○} \text{---} \text{□} \end{array} + \begin{array}{c} \bullet \text{---} \bullet \\ \text{1} \text{---} \text{2} \\ \text{○} \text{---} \text{□} \end{array} + \begin{array}{c} \bullet \text{---} \bullet \\ \text{1} \text{---} \text{2} \\ \text{○} \text{---} \text{□} \end{array} + \dots$$

$$\approx \begin{array}{c} \text{1} \text{---} \text{2} \\ \text{○} \text{---} \text{□} \end{array}$$

$$(5) c_{HH}(3, 2) = \approx \begin{array}{c} \text{3} \text{---} \text{2} \\ \text{□} \text{---} \text{□} \end{array}$$

$$h_{pH}(r) = -\frac{\beta e^2}{4\pi\epsilon r} e^{-\kappa r} \quad \kappa^2 = \frac{e^2 n_H}{4\pi\epsilon kT}$$

$$-\frac{\beta e^2}{4\pi\epsilon r} e^{-\kappa r} + 1 = e^{-\beta\Psi_{pH}(1,2)}$$

$$\Psi_{pH}(r) = \frac{e^2}{4\pi\epsilon r} e^{-\kappa r} \rightarrow \text{Debye-Huckel Potential}$$

In a nanopore none of the above approximations that allow for an easy solution of the Ornstein-Zernicke equation really hold.

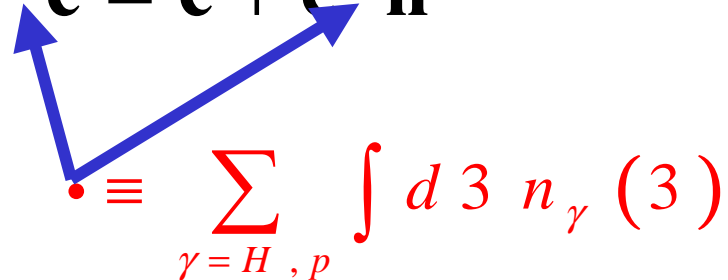
**What can we do?**

## Proof of the Variational Theorem for the Ornstein-Zernicke :-

OZ possesses a general Variational property with regards to **trial** solutions that could be exploited:

$$h_{pH}(1,2) = c_{pH}(1,2) + \sum_{\gamma=H,p} \int d^3 h_{p\gamma}(1,3) n_{\gamma}(3) c_{\gamma H}(3,2)$$

$$\mathbf{h} = \mathbf{c} + \mathbf{h} \cdot \mathbf{c} = \mathbf{c} + \mathbf{c} \cdot \mathbf{h}$$


$$\cdot \equiv \sum_{\gamma=H,p} \int d^3 n_{\gamma}(3)$$

Define functional:  $\mathbf{F}(\mathbf{h}) = \mathbf{h} - \mathbf{c} - \mathbf{h} \cdot \mathbf{c} = \mathbf{0}$

$$\mathbf{F}(\mathbf{h}) = \mathbf{h} - \mathbf{c} - \mathbf{h} \cdot \mathbf{c} = \mathbf{0}$$

Consider a trial solution # 1:  $\mathbf{h}_t$ .

Taylor Expand  $\mathbf{F}(\mathbf{h})$  about  $\mathbf{h}_t$  to linear term:

$$\mathbf{F}(\mathbf{h}) = \mathbf{F}(\mathbf{h}_t) + \left[ \frac{\delta \mathbf{F}(\mathbf{h})}{\delta \mathbf{h}} \right]_{\mathbf{h}=\mathbf{h}_t} \cdot (\mathbf{h} - \mathbf{h}_t) + o(2) = \mathbf{0}$$

Solve for approximate  $\mathbf{h}$

$$\mathbf{h} \approx \mathbf{h}_v = \mathbf{h}_t - \left[ \frac{\delta \mathbf{F}(\mathbf{h})}{\delta \mathbf{h}} \right]_{\mathbf{h}=\mathbf{h}_t}^{-1} \cdot \mathbf{F}(\mathbf{h}_t)$$

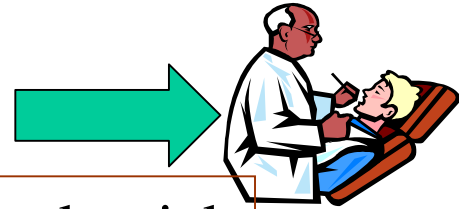
$$\left[ \frac{\delta \mathbf{F}(\mathbf{h})}{\delta \mathbf{h}} \right] = \mathbf{1} - \mathbf{c} \quad \text{Notice: } (\mathbf{1} + \mathbf{h}) \cdot (\mathbf{1} - \mathbf{c}) = \mathbf{1} + (\mathbf{h} - \mathbf{c} - \mathbf{h} \cdot \mathbf{c}) = \mathbf{1} + \mathbf{F}(\mathbf{h}) = \mathbf{0}$$

$$\therefore \left[ \frac{\delta \mathbf{F}(\mathbf{h})}{\delta \mathbf{h}} \right]^{-1} = (\mathbf{1} + \mathbf{h}) \rightarrow (\mathbf{1} + \mathbf{h}_t); \mathbf{h}_t = \text{Trial solution \#2}$$

$h_t$  and  $h_\tau$  can have same form

$$\mathbf{h} \approx \mathbf{h}_v = \mathbf{h}_t - \left[ \frac{\delta \mathbf{F}(\mathbf{h})}{\delta \mathbf{h}} \right]_{\mathbf{h}=\mathbf{h}_t}^{-1} \cdot \mathbf{F}(\mathbf{h}_t) = \mathbf{h}_t - (\mathbf{1} + \mathbf{h}_\tau) \cdot \mathbf{F}(\mathbf{h}_t) =$$

$$\mathbf{h}_v = \mathbf{c} + \mathbf{h}_t \cdot \mathbf{c} - \mathbf{h}_t \cdot \mathbf{h}_\tau + \mathbf{c} \cdot \mathbf{h}_\tau + \mathbf{h}_t \cdot \mathbf{c} \cdot \mathbf{h}_\tau$$



Looks sick



There is hope!

$\mathbf{h}_v$  possesses a "stationary point" when  $\mathbf{h}_t = \mathbf{h}$  (exact) and  $\mathbf{h}_\tau = \mathbf{h}$  (exact):

$$\left[ \frac{\delta \mathbf{h}_v}{\delta \mathbf{h}_t} \right]_{\substack{\mathbf{h}_t = \mathbf{h} \\ \mathbf{h}_\tau = \mathbf{h}}} = \mathbf{c} - \mathbf{h} + \mathbf{c} \cdot \mathbf{h} = \mathbf{F}(\mathbf{h}) = 0$$

$$\left[ \frac{\delta \mathbf{h}_v}{\delta \mathbf{h}_\tau} \right]_{\substack{\mathbf{h}_t = \mathbf{h} \\ \mathbf{h}_\tau = \mathbf{h}}} = \mathbf{c} - \mathbf{h} + \mathbf{h} \cdot \mathbf{c} = \mathbf{F}(\mathbf{h}) = 0$$

Q.E.D.

# Question

How can we make use of this result?

Take parametrized trial solutions:

$$\mathbf{h}_v = \mathbf{c} + \mathbf{h}_t \cdot \mathbf{c} - \mathbf{h}_t \cdot \mathbf{h}_\tau + \mathbf{c} \cdot \mathbf{h}_\tau + \mathbf{h}_t \cdot \mathbf{c} \cdot \mathbf{h}_\tau$$

$\mathbf{h}_t(a_1, a_3, \dots, a_M)$

$\mathbf{h}_\tau(b_1, b_3, \dots, b_M)$

$\mathbf{h}_v(a_1, a_3, \dots, a_M, b_1, b_3, \dots, b_M)$

$$\left( \frac{\partial \mathbf{h}_v}{\partial a_j} \right) = 0; \quad j = 1, 2 \dots M, \quad \left( \frac{\partial \mathbf{h}_v}{\partial b_j} \right) = 0; \quad j = 1, 2 \dots M$$

Work completed

R. Paul and S. J. Paddison Phys. Rev. E, **67**, 016108, (2003)

Returning to our screened potential calculation:

$$h_t(r, a) = h_\tau(r, a) = -\frac{\beta e^2}{4\pi\epsilon r} e^{-ar}$$

The parameter  $a$  is the new screening constant and is the variational parameter.



Variationally calculate  $a_{\text{Best}}$



Calculate  $h_{v;pH}(1, 2, a_{\text{Best}})$



$$g_{pH}(1, 2, a_{\text{Best}}) = h_{v;pH}(1, 2, a_{\text{Best}}) + 1$$



$$\Psi_{pH}(1, 2) = -(1/\beta) \ln [g_{pH}(1, 2, a_{\text{Best}})]$$

# Question

Is there a testing ground available where the practical usefulness of the variational method can be explored?

**Hard-Sphere Fluid Model!!! Not in a Nanopore.**

## Testing Approach:-

(1) OZ Equation:

$$h(\vec{r}_1, \vec{r}_2) = c(|\vec{r}_1 - \vec{r}_2|) + n \int d\vec{r}_3 c(|\vec{r}_1 - \vec{r}_3|) h(\vec{r}_3, \vec{r}_2)$$

(2) Start with the  $c$  of Wertheim for hard-sphere fluids (Phys. Rev. Letters, **10**, 321 (1963)):

$$c(|\vec{r}_1 - \vec{r}_2|) = -H(\sigma - |\vec{r}_1 - \vec{r}_2|) \frac{1}{\sigma^3} (\lambda_0 + \lambda_1 |\vec{r}_1 - \vec{r}_2| + \lambda_1 |\vec{r}_1 - \vec{r}_2|^3)$$

(3) Calculate  $h(\vec{r}_1, \vec{r}_2)$  using the variational approach.

(4) For a hard sphere fluid  $h(|\vec{r}_1 - \vec{r}_2|) = -1$  when  $|\vec{r}_1 - \vec{r}_2| < \sigma$ .

$|h(|\vec{r}_1 - \vec{r}_2|)|$  is maximum in  $|\vec{r}_1 - \vec{r}_2| < \sigma$ .

$\therefore$  Test for variational approach and test function is the ability to reproduce this result.

We select extremely simple trial functions of the same form:

$$h_t \left( \left| \vec{r}_i - \vec{r}_j \right| \right) = h_\tau \left( \left| \vec{r}_i - \vec{r}_j \right| \right) = -aH \left( \sigma - \left| \vec{r}_i - \vec{r}_j \right| \right)$$

$a =$  Variational Parameter.

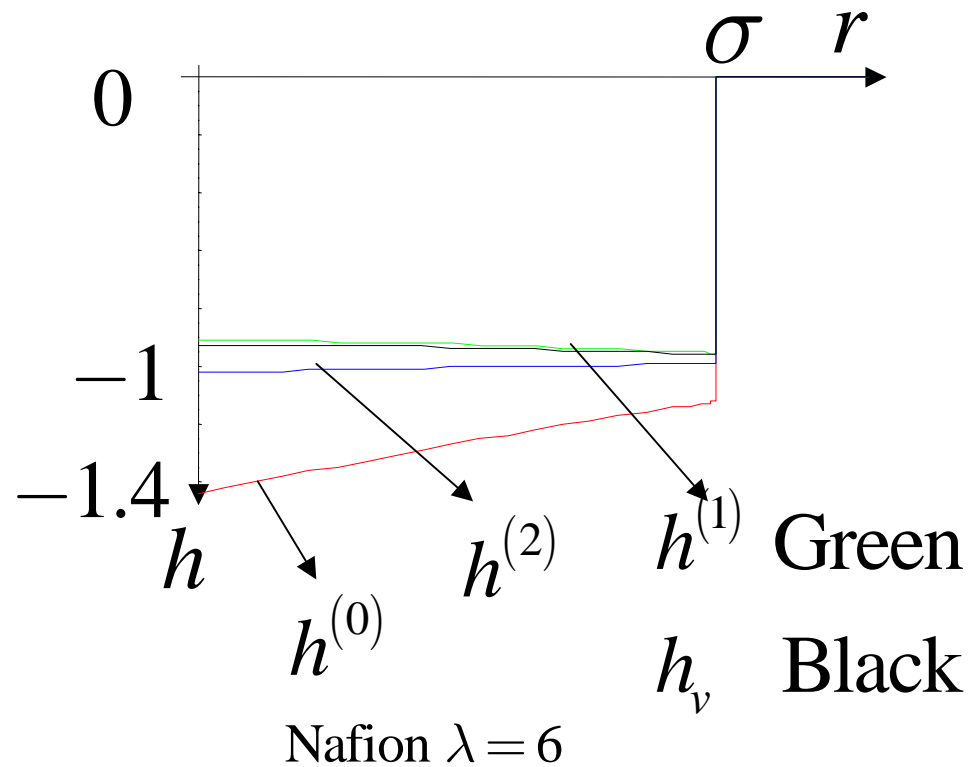
For purposes of comparison we also include three approximate solutions that are obtained from an iterative expansion of the Ornstein-Zernicke equation:

$\mathbf{h} = \mathbf{c} + \mathbf{c} \cdot \mathbf{h} = \mathbf{c} + \mathbf{c} \cdot \mathbf{c} + \mathbf{c} \cdot \mathbf{c} \cdot \mathbf{c} + \dots \rightarrow$  Ornstein-Zernicke Equation.

$$\mathbf{h}^{(0)} = \mathbf{c}$$

$$\mathbf{h}^{(1)} = \mathbf{c} + \mathbf{c} \cdot \mathbf{c}$$

$$\mathbf{h}^{(2)} = \mathbf{c} + \mathbf{c} \cdot \mathbf{c} + \mathbf{c} \cdot \mathbf{c} \cdot \mathbf{c}$$



Verdict: Reasonably good performance from simple trial function.

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## Conclusions:-

The variational method does provide us with yet another tool that can be used for obtaining approximate solutions of the OZ equation.

- (1) We are able to take results (exact or approximate) obtained in simple environments and extend them to more difficult situations.
- (2) It is possible to use simple trial functions and obtain analytic results or reduce the amount of computation time.