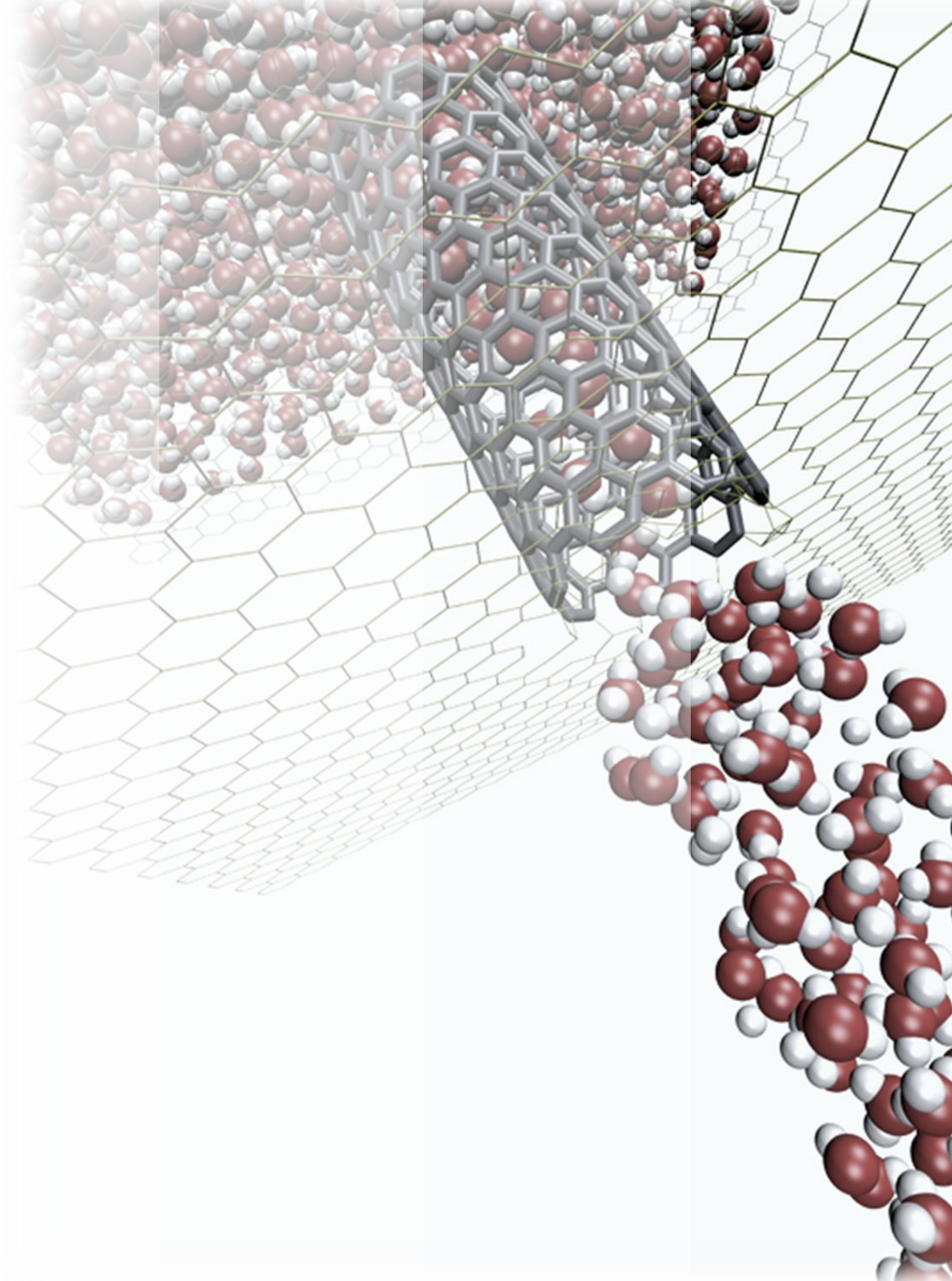
Monte Carlo simulation of coarse-grained model for Halloysite Nanotube

Hye-jeong Cheon

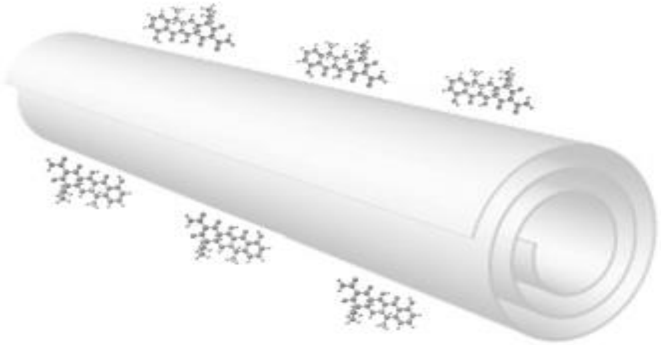
Department of Physics, NTNU, Trondheim

14. Sep. 2018



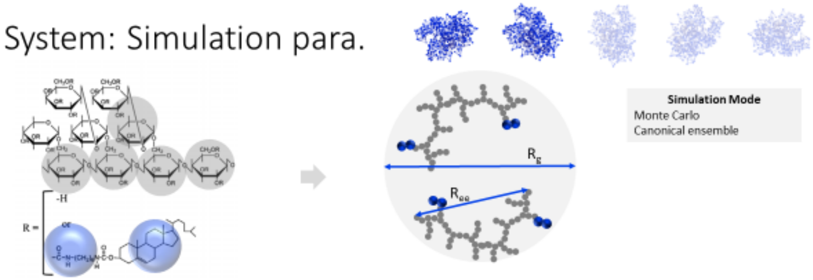
Monte Carlo simulation of coarse-grained system

Understanding molecules by computation

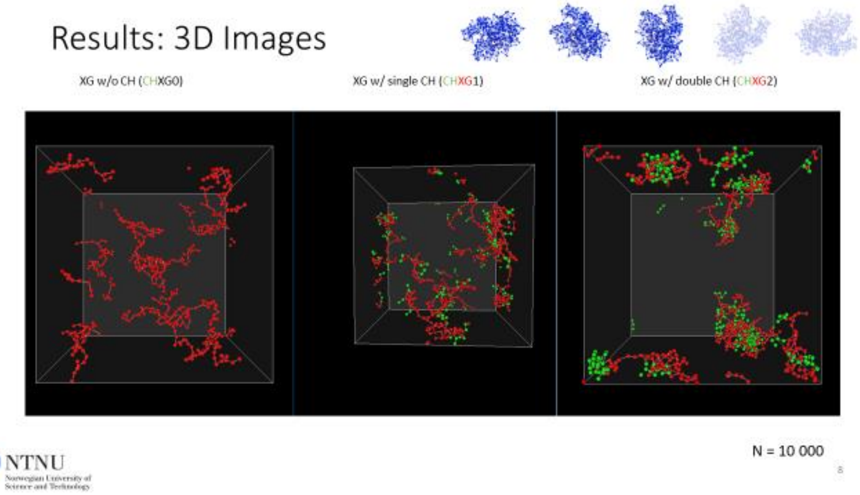


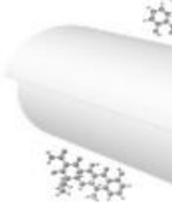
Monte Carlo simulation of coarse-grained system

Nanogel

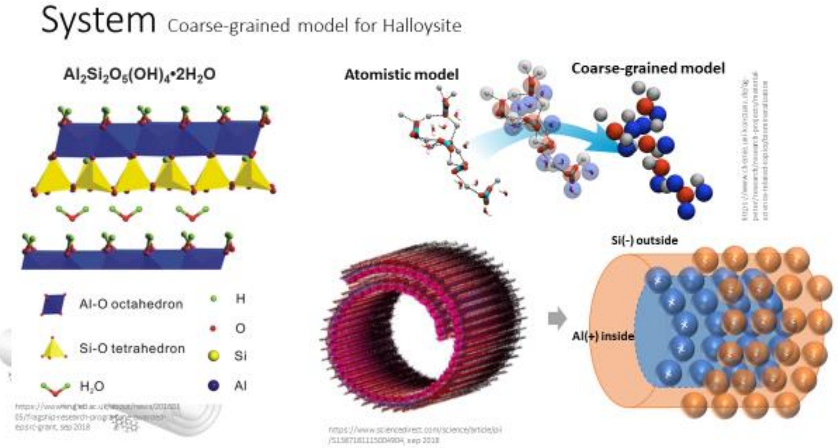


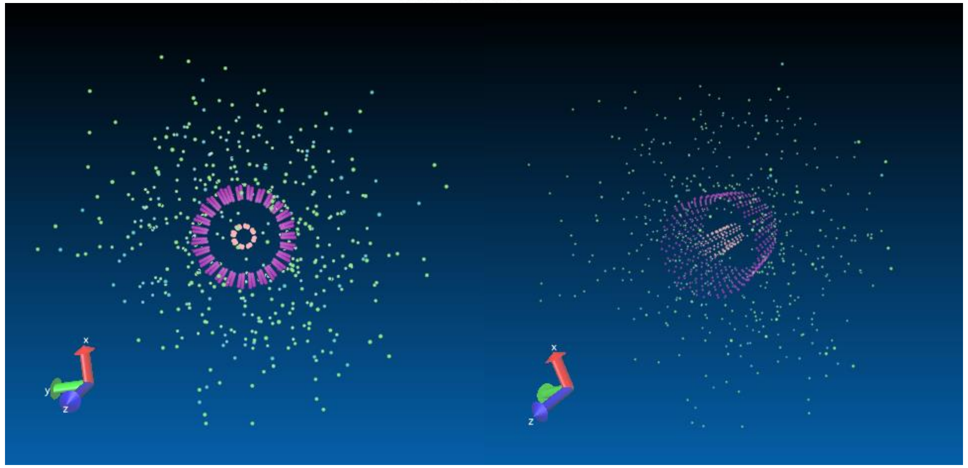
	Parameters for Simulation							
Parameter	nct	npptct(1,1)	Npptct(1,2)	npt	nppt	natpt	massat	radat
Units	#	→	→	→	→	→	g/mol	Å
XG w/o CH (CHXG0)	2	50,0	**2,0**	2	560,0	1,1	10.0	2.0
XG w/ single CH (CHXG1)	2	50,0	**2,2**	2	560,160	1,1	10.0	2.0





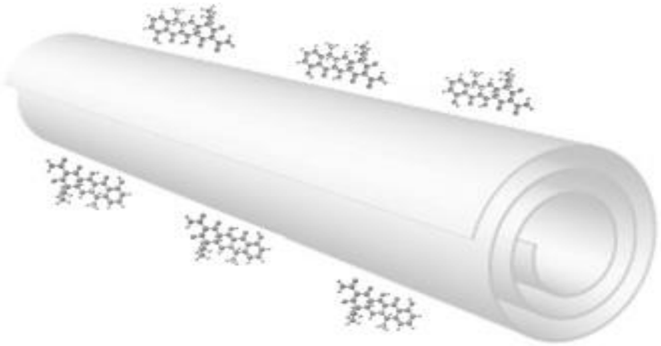
Nanotube





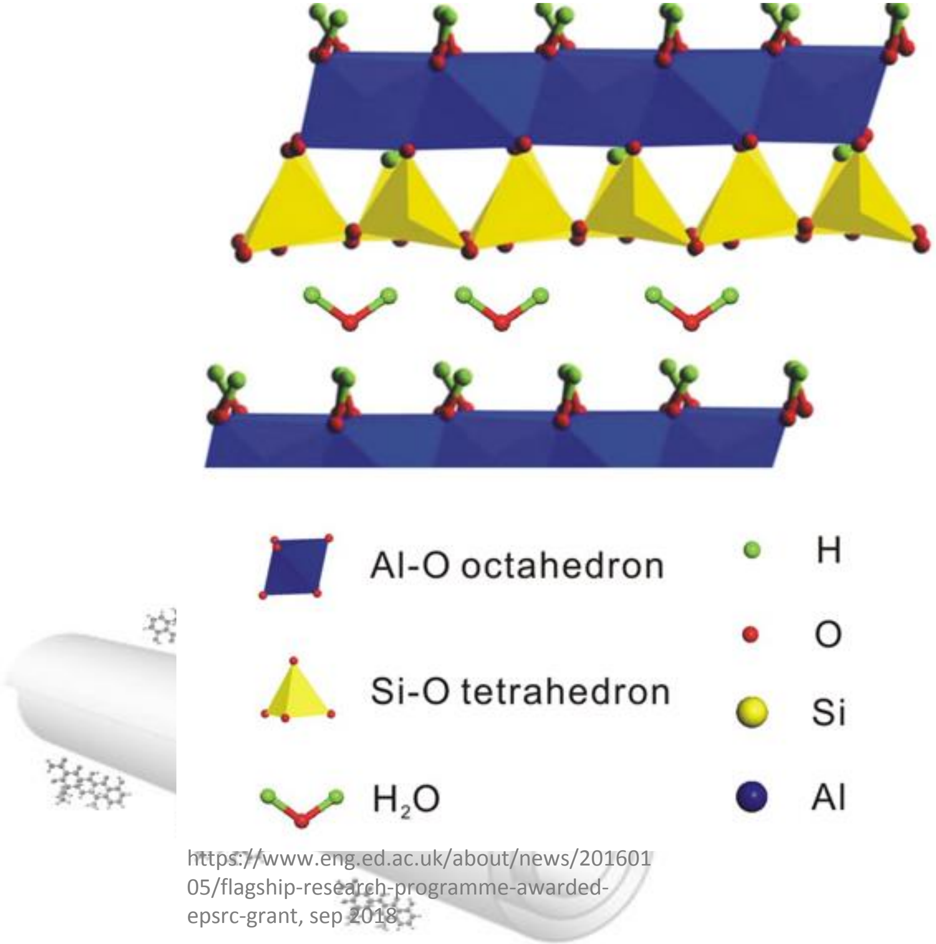
Halloysite Nanotube

Halloysite Nanotube structure and modelling system



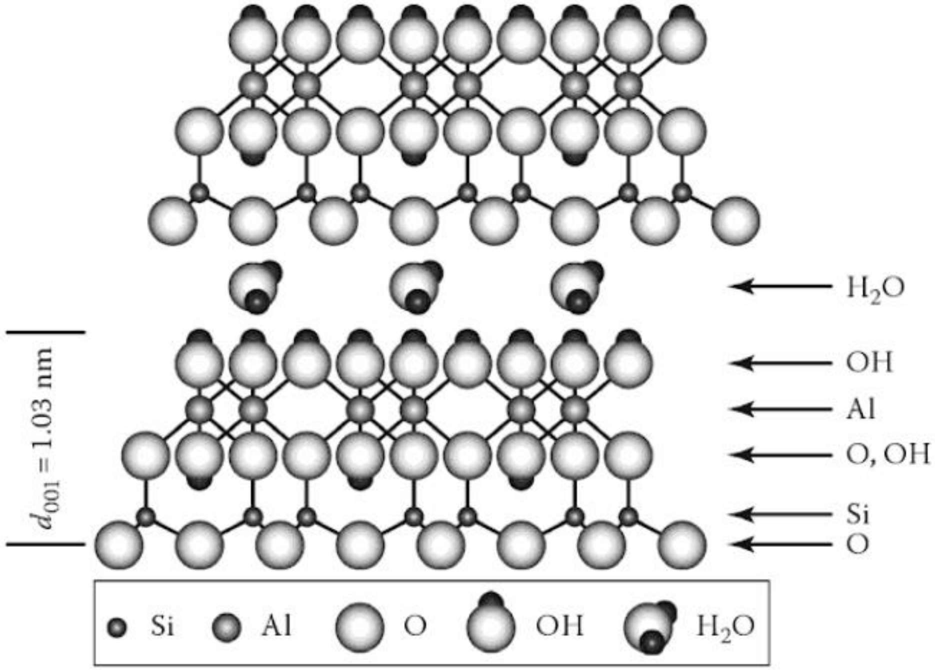
Halloysite structure and property

$Al_2Si_2O_5(OH)_4 \cdot 2H_2O$



https://www.eng.ed.ac.uk/about/news/20160105/flagship-research-programme-awarded-epsrc-grant, sep 2018

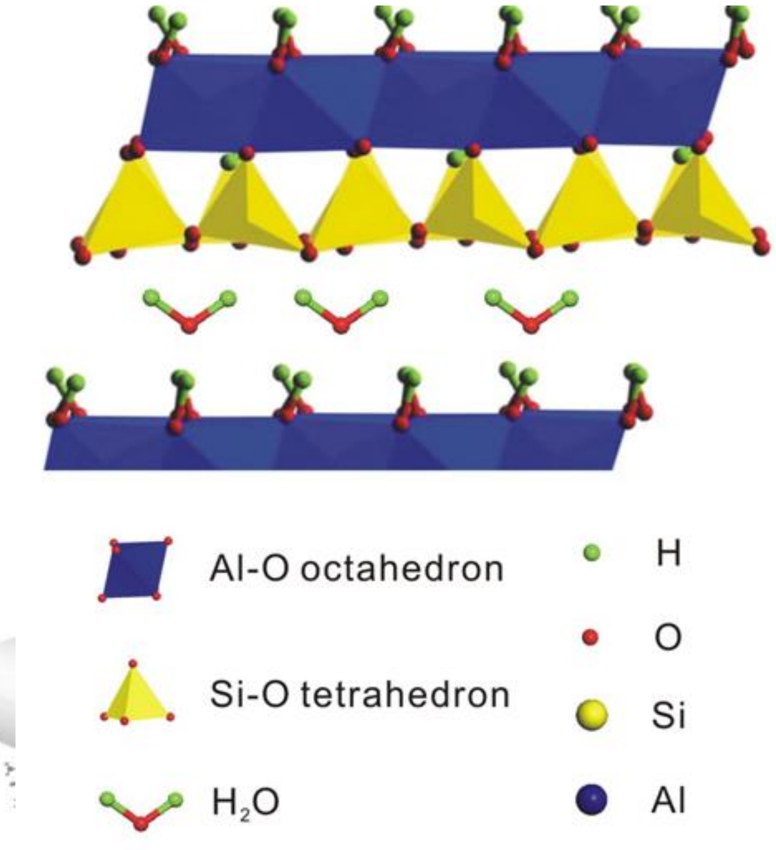
Sheet becomes tube
: Inside(Al) and Outside (Si)



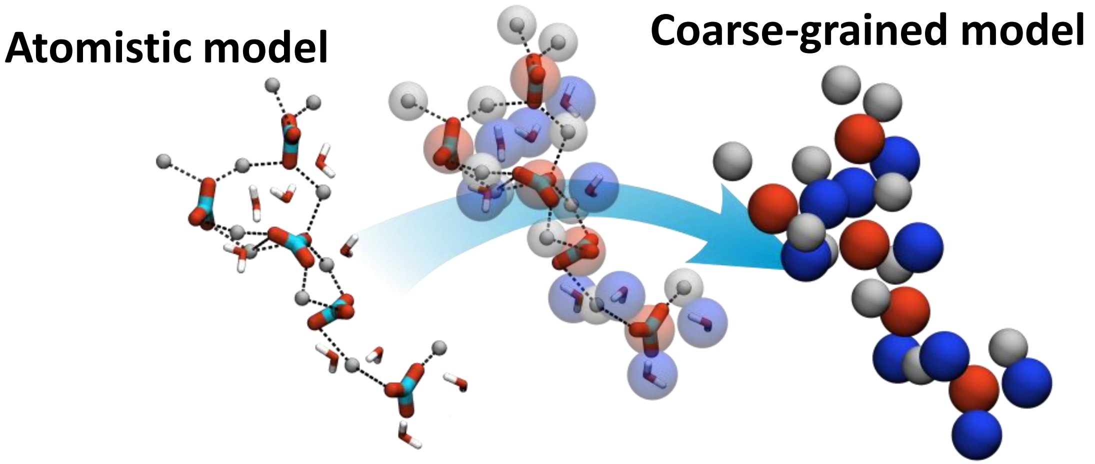
Soil and Water Chemistry: An Integrative Approach, Second Edition, Av Michael E. Essington, p86

System Coarse-grained model for Halloysite

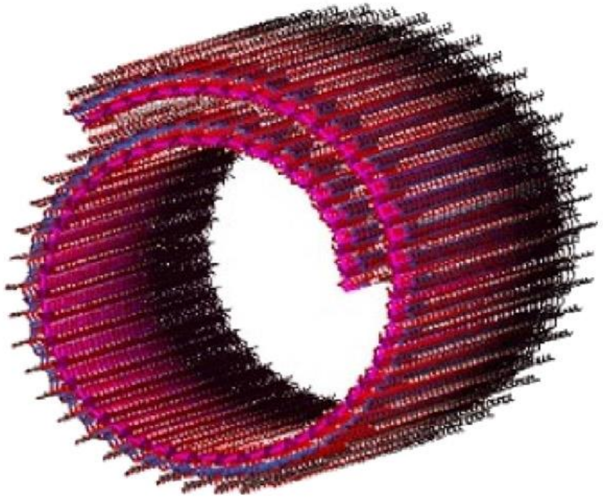
$Al_2Si_2O_5(OH)_4 \cdot 2H_2O$



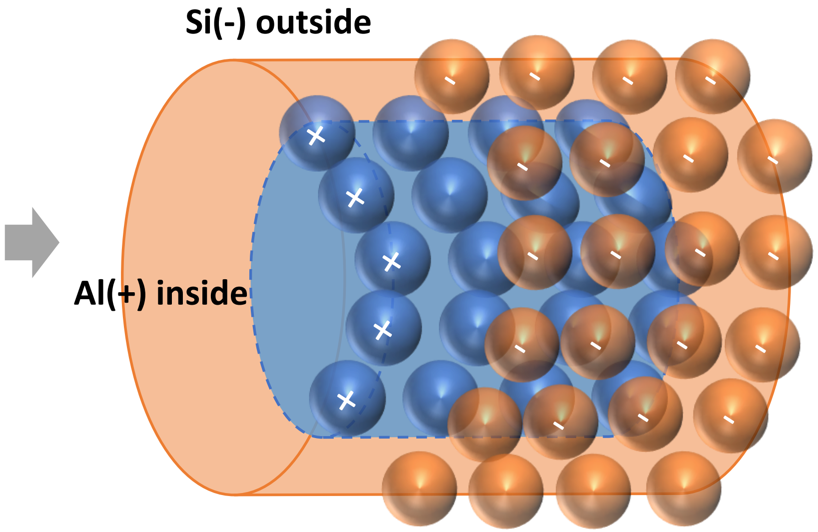
https://www.eng.ed.ac.uk/about/news/20160105/flagship-research-programme-awarded-epsrc-grant, sep 2018



https://www.chemie.uni-konstanz.de/ag-peter/research/research-projects/material-science-related-topics/biomineralization

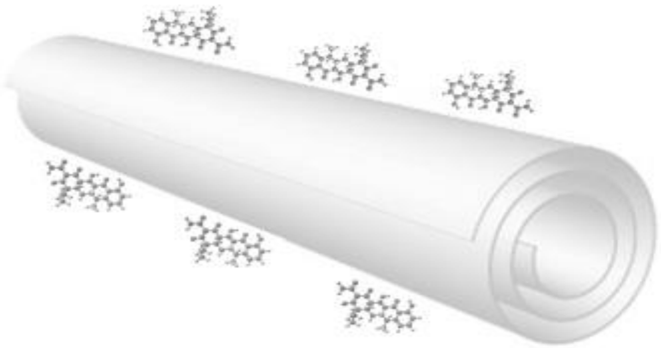


https://www.sciencedirect.com/science/article/pii/S1387181115004904, sep 2018



Halloysite Nanotube

Simulation with different thickness and number of particles



Modelling parameter for simulation

	Number of atom		Nanotube structure			Radius of atom		Cylinder system structure		Dissociation constant		Remarks
	# Al	**# Si**	**Thickness Al-Si [Å]**	**Inner radius [Å]**	**Length [Å]**	**Rad Al [Å]**	**Rad Si [Å]**	**Cylinder rad [Å]**	**Cylinder length [Å]**	**pK(Al)**	**pK(Si)**	
Parameter	**nppt(Al)**	**nppt(Si)**	**dcap**	**rcap**	**lcap**	**radat(Al)**	**radat(Si)**	**cylrad**	**cyllen**	**pK(1)**	**pK(3)**	
Same # atom, different thickness	100	400	100	60	700	2.0	2.0	800	1200	9	4.2	
	100	**400**	**180**	**60**	700	**2.0**	**2.0**	800	1200	**9**	**4.2**	Standard
	100	400	240	60	700	2.0	2.0	800	1200	9	4.2	
	100	400	500	60	700	2.0	2.0	800	1200	9	4.2	
Same charge, different thickness	100	267	100	60	700	2.0	2.0	800	1200	9	4.2	
	100	500	240	60	700	2.0	2.0	800	1200	9	4.2	
	100	933	500	60	700	2.0	2.0	800	1200	9	4.2	
Comparing with Al+Si NT and Al/Si NT	100	-	-	60	700	2.0	-	800	1200	9	-	
	-	400	180	60	700	-	2.0	800	1200	-	4.2	

Modelling parameter for simulation

	Number of atom		Nanotube structure			Remarks
	# Al	# Si	Thickness Al-Si [Å]	Inner radius [Å]	Length [Å]	
Parameter	**nppt(Al)**	**nppt(Si)**	**dcap**	**rcap**	**lcap**	
Same # atom, different thickness	100	400	100	60	700	Standard
	100	**400**	**180**	**60**	700	
	100	400	240	60	700	
	100	400	500	60	700	
Same charge, different thickness	100	267	100	60	700	
	100	500	240	60	700	
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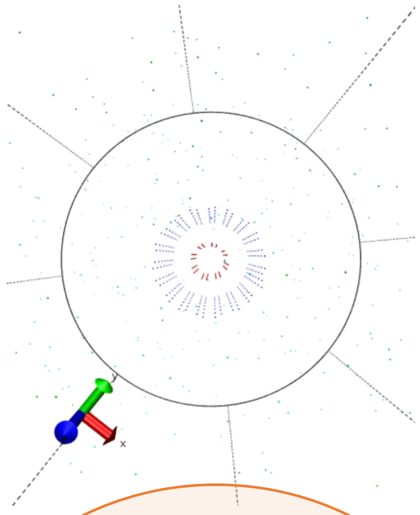
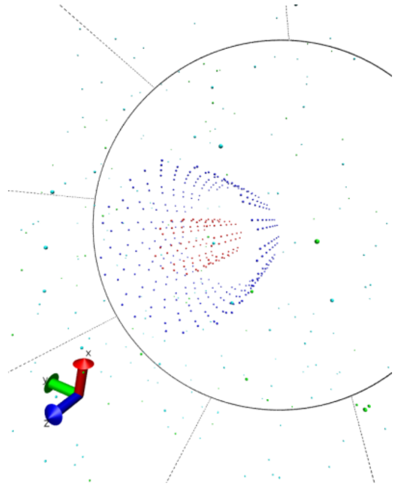
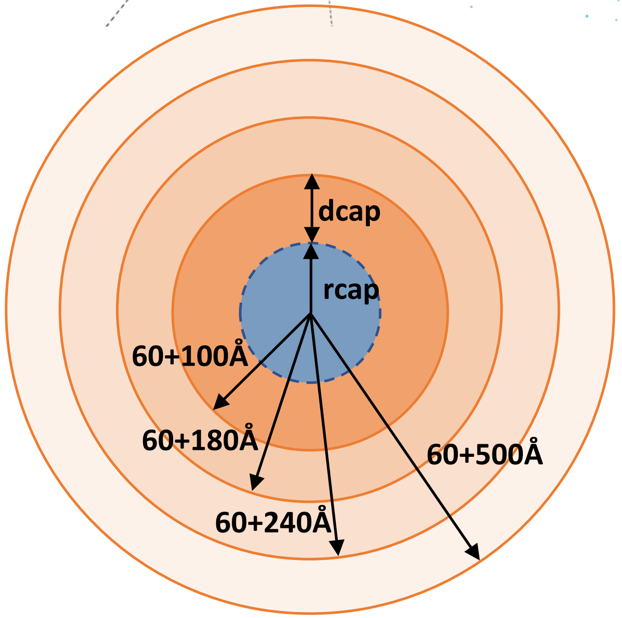
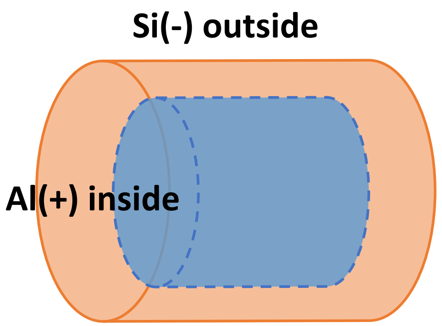


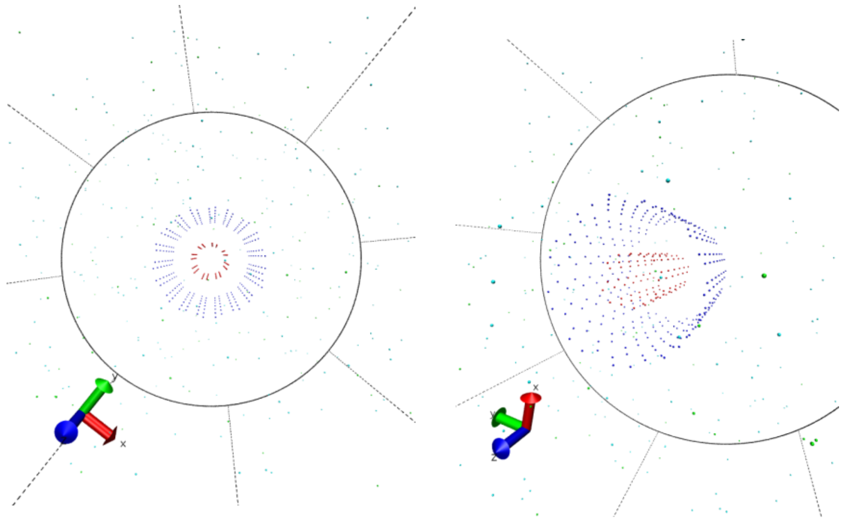


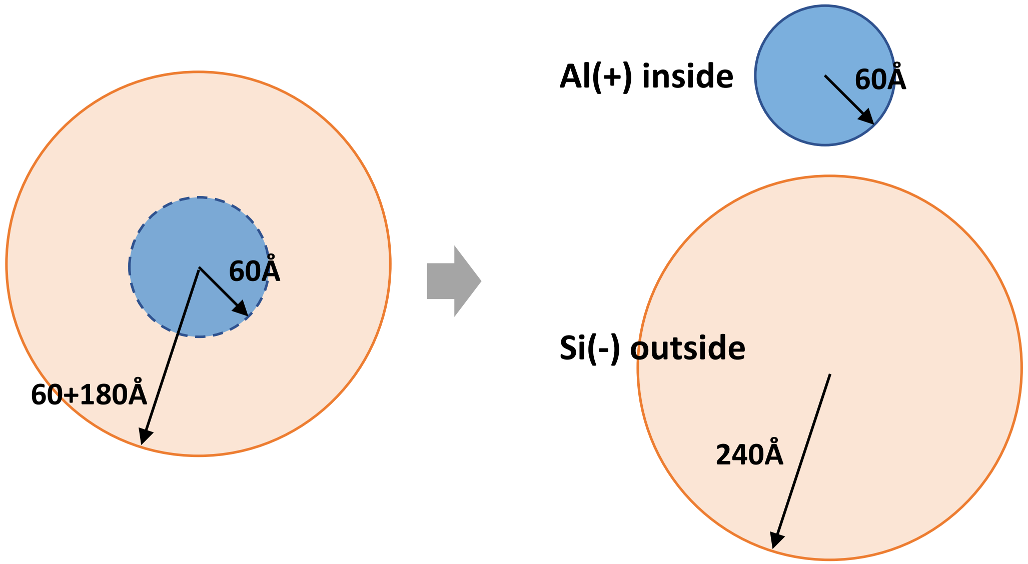




Modelling parameter for simulation

	Number of atom		Nanotube structure			Remarks
	# Al	**# Si**	**Thickness Al-Si [Å]**	**Inner radius [Å]**	**Length [Å]**	
Parameter	**nppt(Al)**	**nppt(Si)**	**dcap**	**rcap**	**lcap**	
Same # atom, different thickness	100	400	100	60	700	
	100	**400**	**180**	**60**	700	Standard
	100	400	240	60	700	
	100	400	500	60	700	
Same charge, different thickness	100	267	100	60	700	
	100	500	240	60	700	
	100	933	500	60	700	
Comparing with Al+Si NT and Al/Si NT	100	-	-	60	700	
	-	400	180	60	700	





Modelling parameter for simulation

	Number of atom		Nanotube structure			Remarks
	# Al	# Si	Thickness Al-Si [Å]	Inner radius [Å]	Length [Å]	
Parameter	nppt(Al)	nppt(Si)	dcap	rcap	lcap	
Same # atom, different thickness	100	400	100	60	700	Standard
	100	**400**	**180**	**60**	700	
	100	400	240	60	700	
	100	400	500	60	700	
Same charge, different thickness	100	267	100	60	700	
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Comparing with Al+Si NT and Al/Si NT	100	-	-	60	700	
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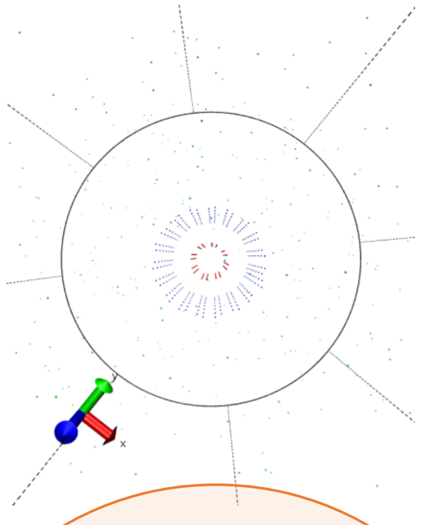
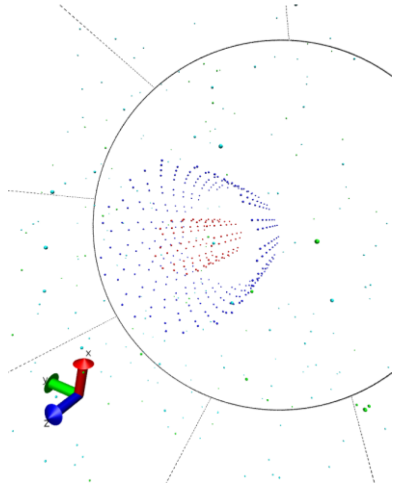
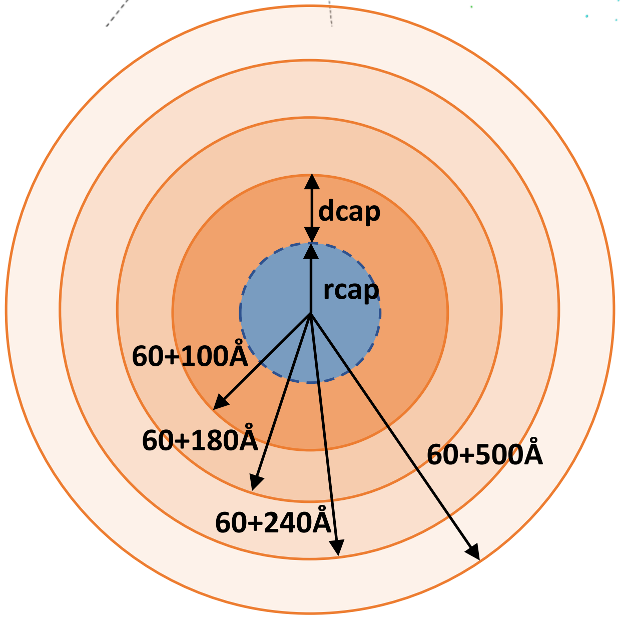
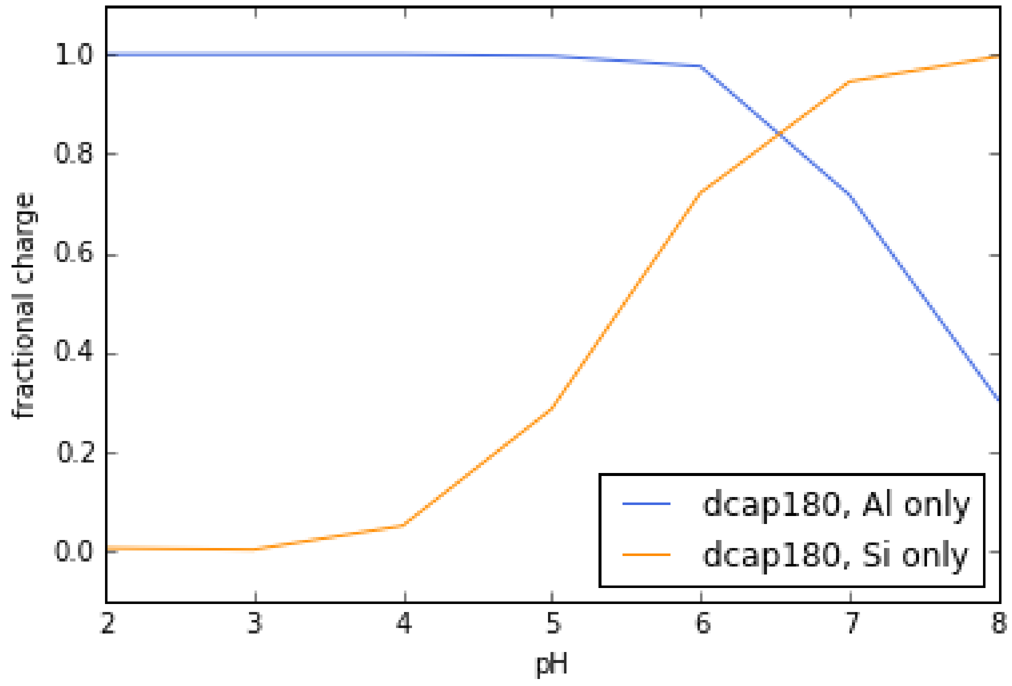




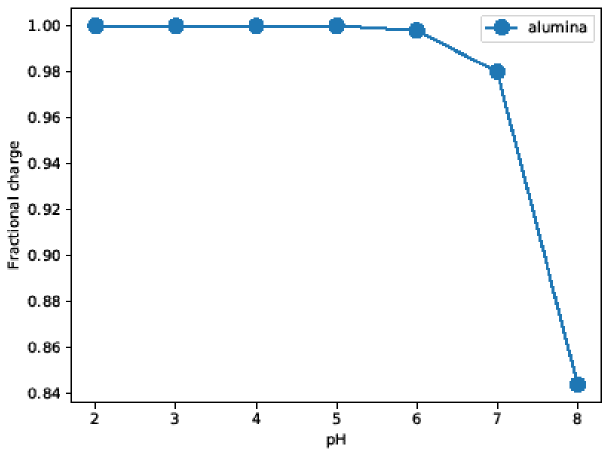


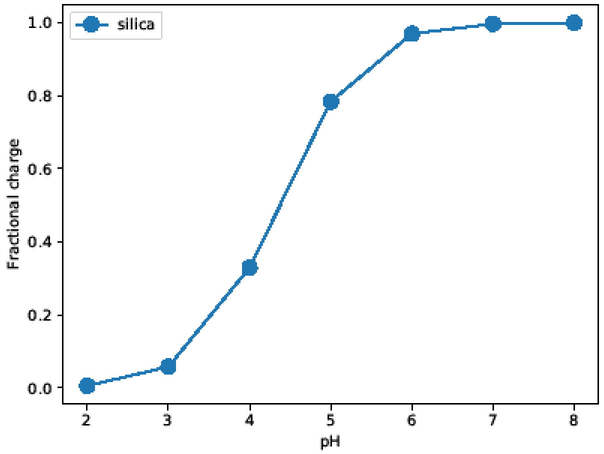
$$\sigma_{inner} (= \sigma_{outer}) = 3.789\text{x}10^{-4}\ charge/\text{Å}^2$$
$$(fixed\ surface\ charge)$$

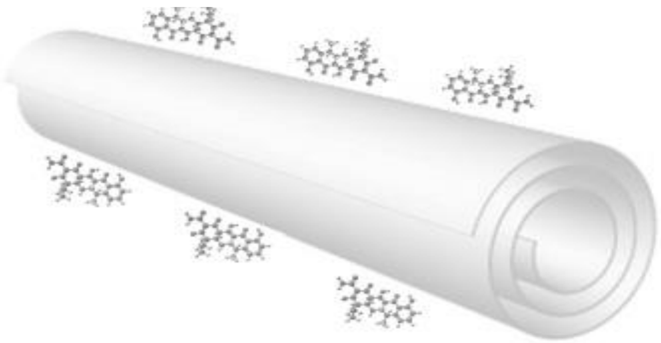
Result titration curve with increasing pH, Al only & Si Only separately



From Constanza

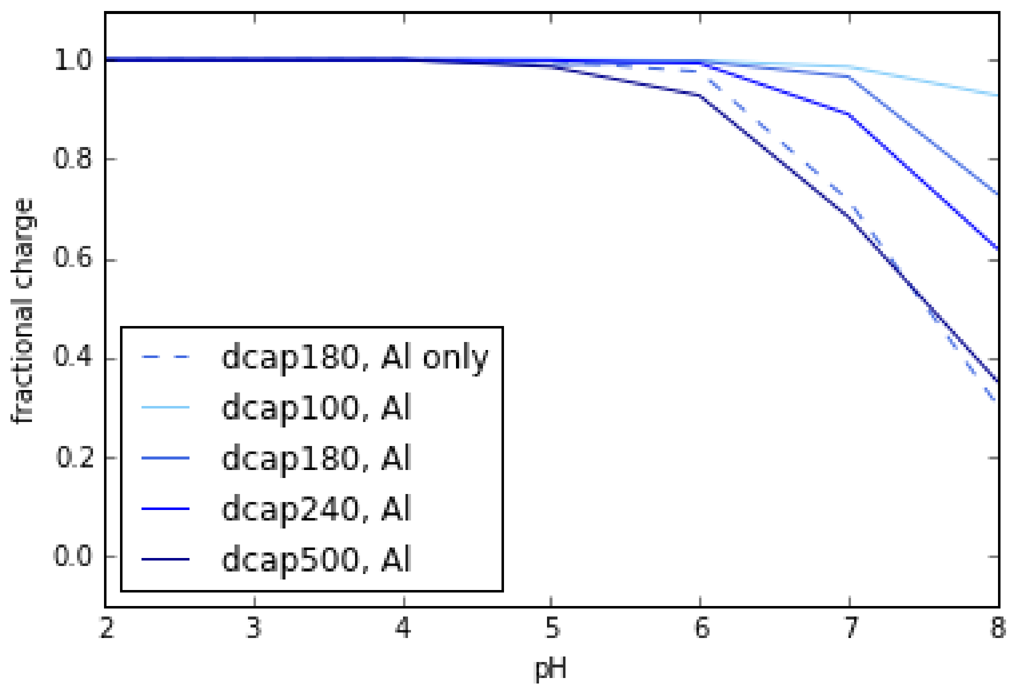


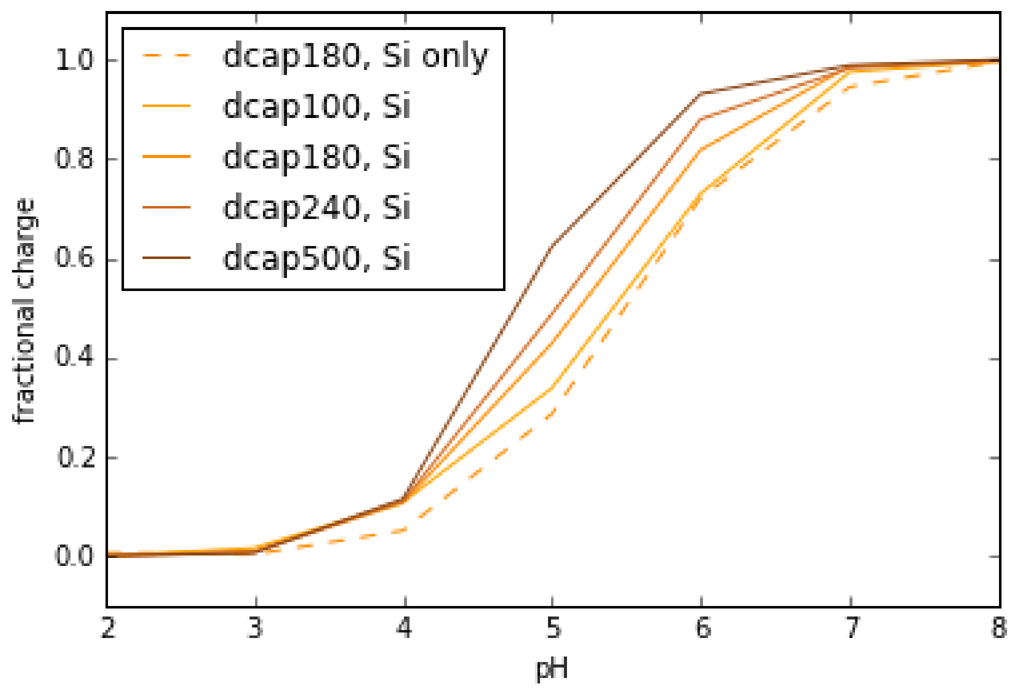


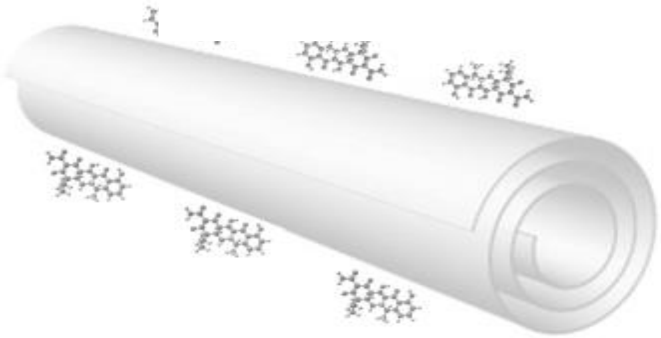


- ✓ Low pH : HA + H_2O → A^- + H_3O^+
- ✓ High pH : B + H_2O → BH^+ + OH^-
- ✓ For finding the most suitable dcap(thickness) **without mutual interaction** btw Al & Si

Result titration curve with increasing pH, same # of atoms



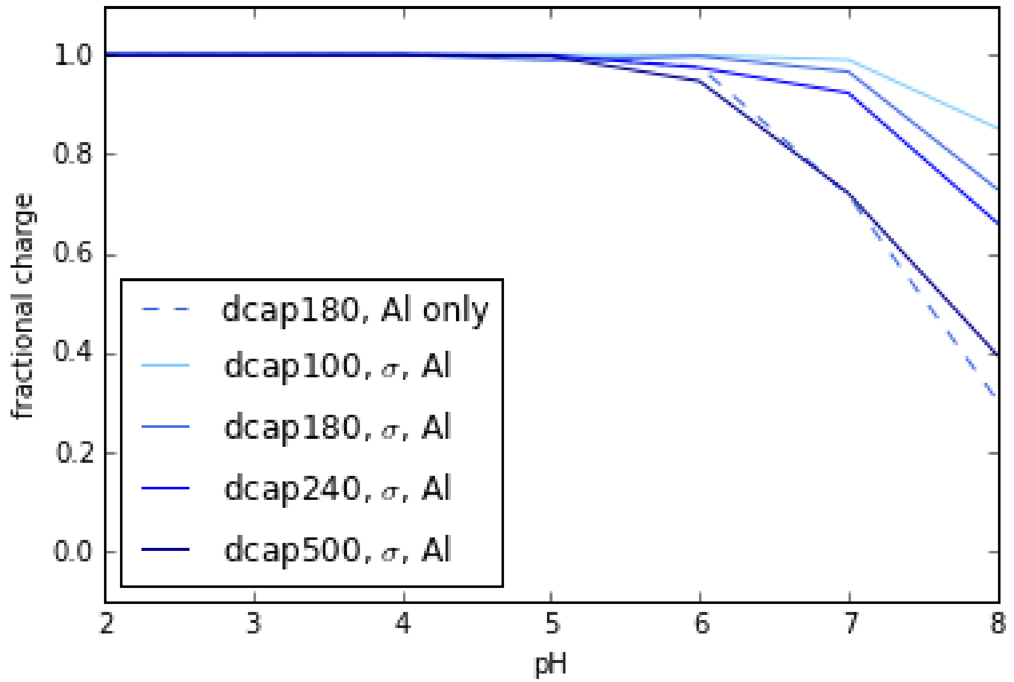


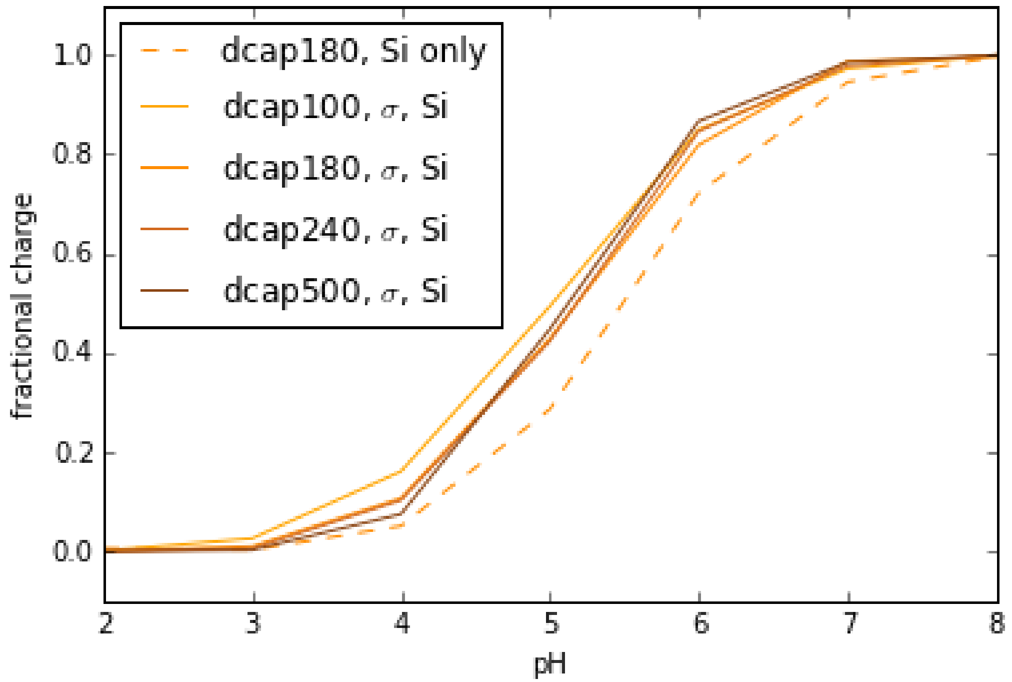


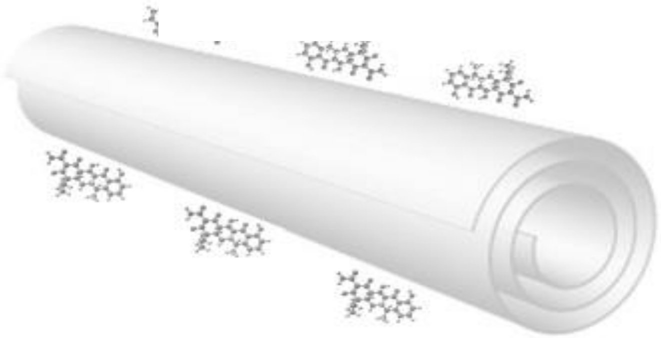
- ✓ Al : titration curve with **dcap500Å ≈ the most suitable**
- ✓ Si : titration curve with **dcap100Å ≈ the most suitable**

  → because of lack of Si beads

Result titration curve with increasing pH, same surface charge($\sigma_{in} = \sigma_{out}$)





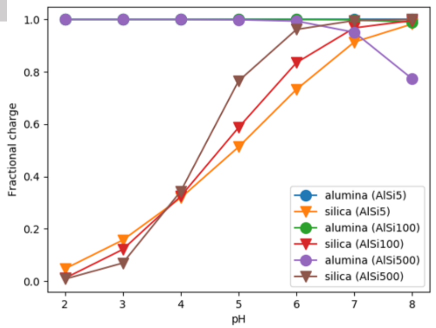


✓ Both Al, Si : system with **dcap500Å ≈ the most suitable** system

Conclusion and future work

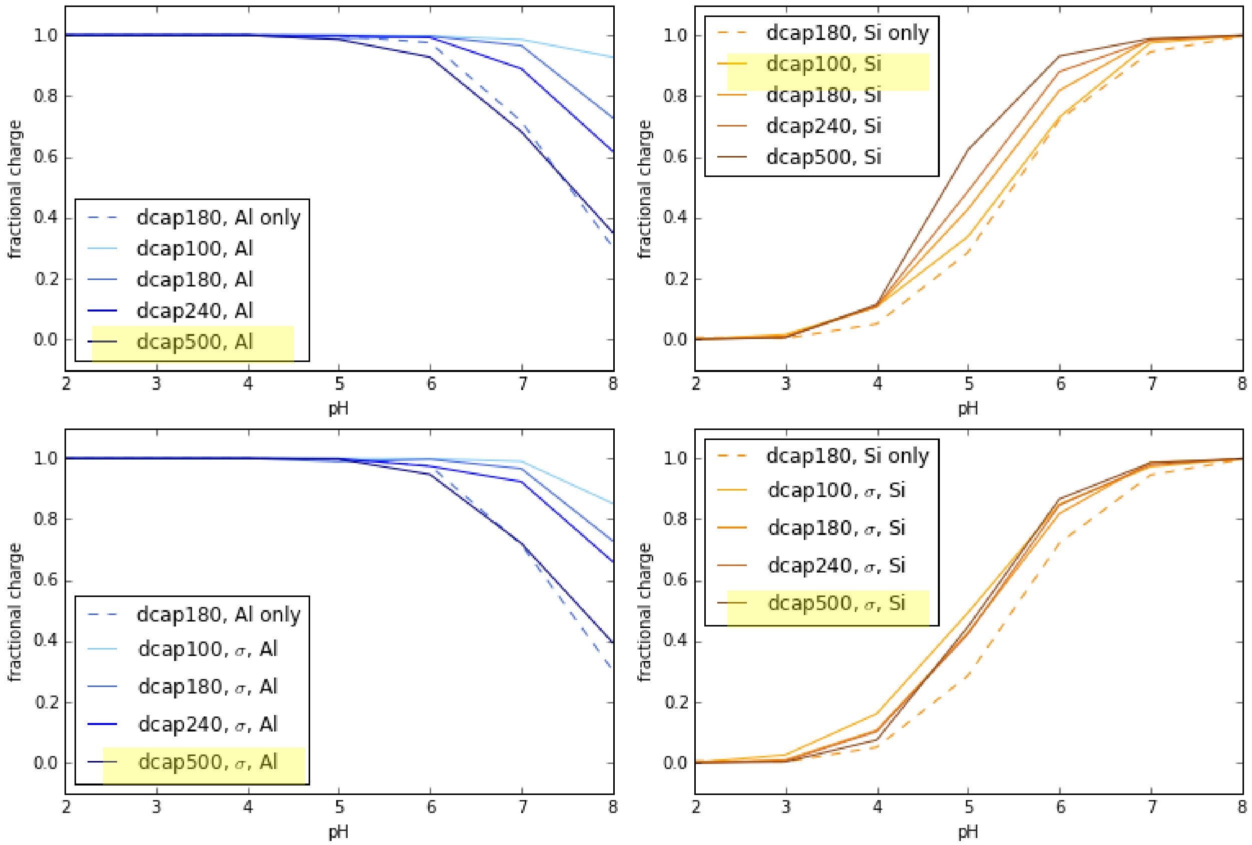
From Costanza

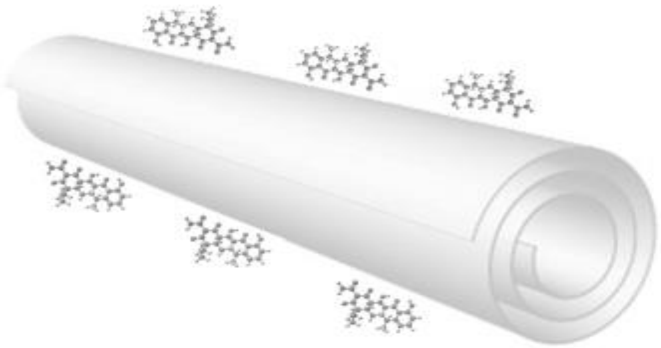
Titration of three systems with different thickness (**dcap**) :
5 Å, 100 Å, 500 Å



By changing the thickness of nanotube is possible to see how the dcap influences the titration.

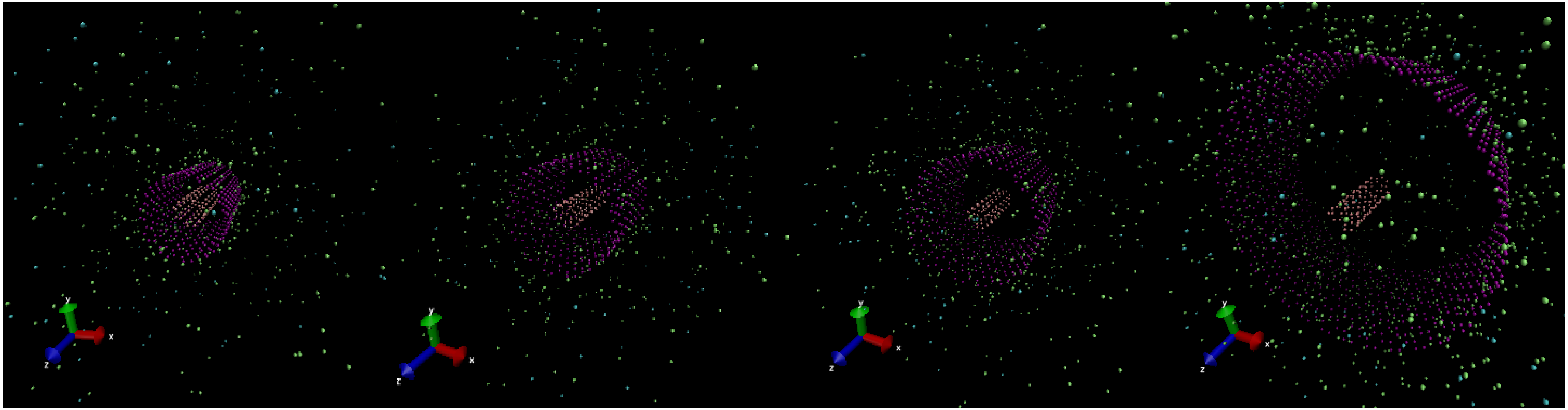
- Increasing the thickeness the interactions between **Al** and **Si** particles is weaker and the titration became more slow and easy.
- The titration curve of the 500 Å dcap system looks like the titration curve of the systems of Al and Si alone without mutual interections.



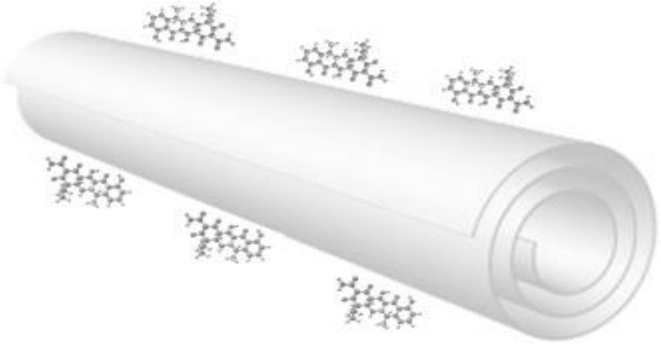


- ✓ Minimize charge effect of Al-Si itself within nanotube
  → large dcap (thickness)
- ✓ Why are two cases above different?
- ✓ Implement nanotube with charged polymers

Result snapshots of 4 dcap lengths(100, 180, 240, 500)



100 **180** **240** **500**



- ✓ dcap500 : not suitable considering btw cell size
  (cell : 800*1200, NT 2)
- ✓ The second suitable condition = **dcap240**

Conclusion and future work

From Costanza

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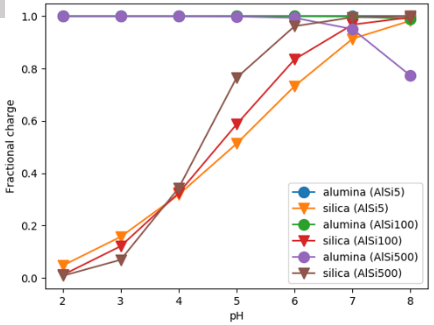
5 Å, 100 Å, 500 Å



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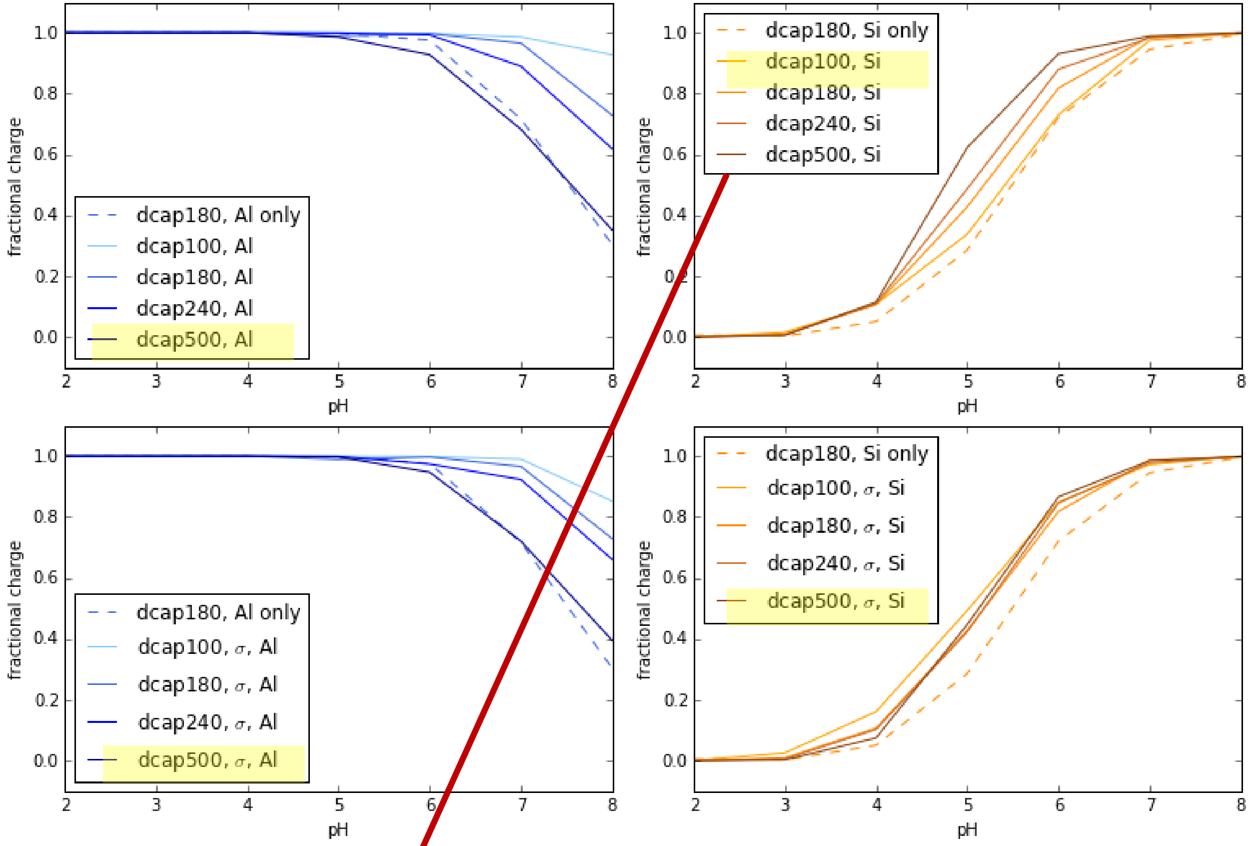
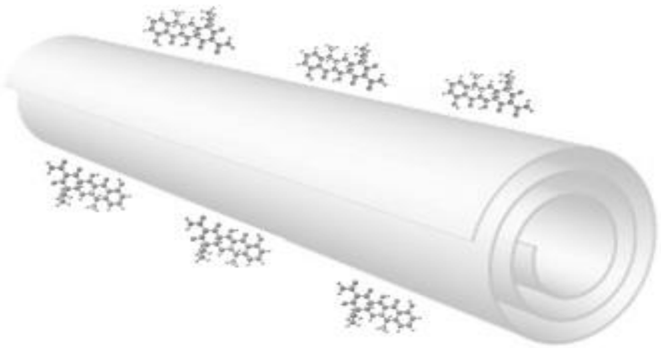
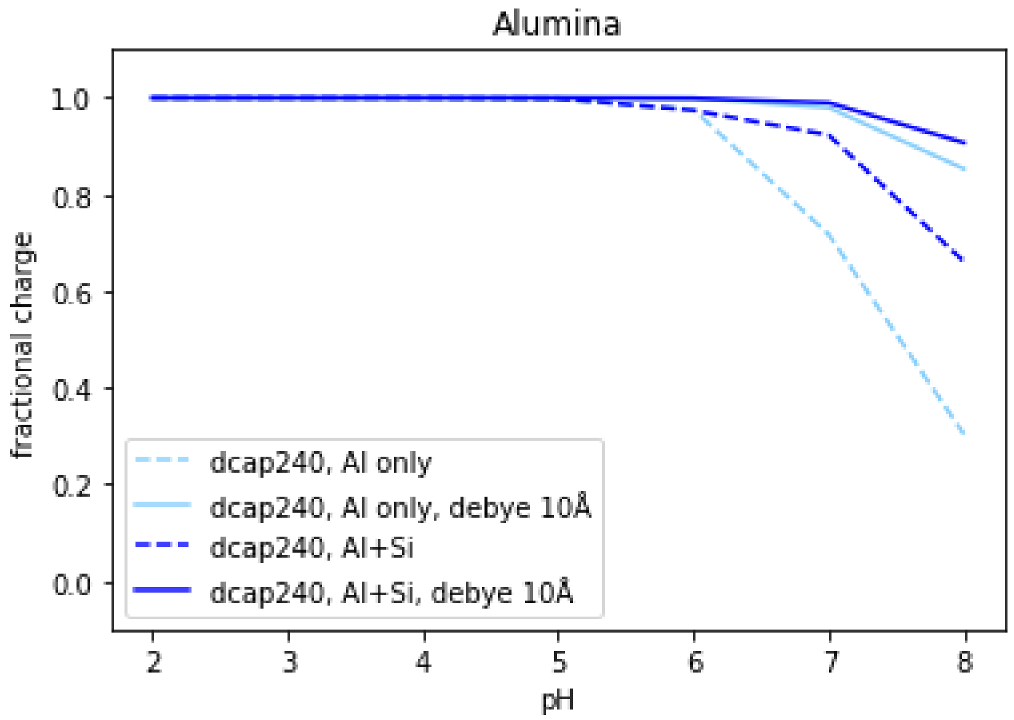
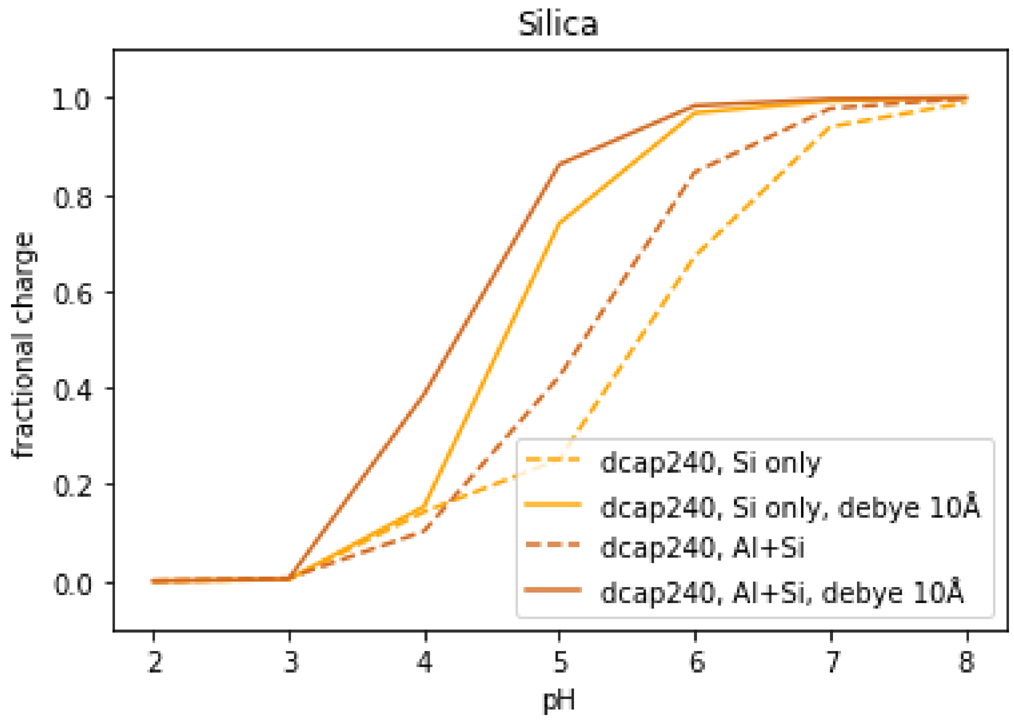


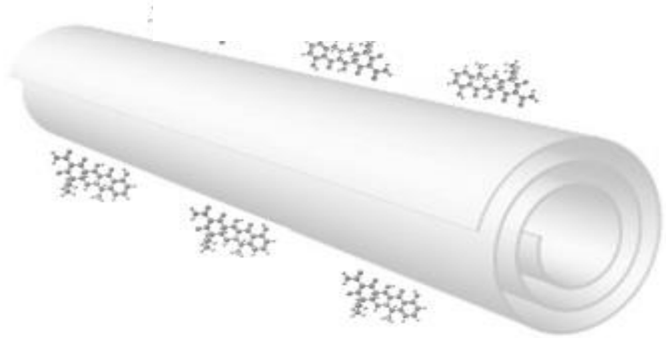


- ✓ Why are two cases above different?
  → for larger dcap, not enough number of Si outside (lower charge density)
- ✓ Need more Si beads
  → Maintain surface charge density(

Result titration curve with same surface charge($\sigma_{in} = \sigma_{out}$), dcap240, debye length 10Å







- ✓ Debye length(adding more ions) : for lowering interference
- ✓ Al : ions

Reference titration curve with increasing pH, same # of atoms

1. Images
1-1. https://www.eng.ed.ac.uk/about/news/20160105/flagship-research-programme-awarded-epsrc-grant, sep 2018
1-2. https://www.sciencedirect.com/science/article/pii/S1387181115004904, sep 2018
1-3. Development of a coarse-grained model for calcium minerals, Computational and Theoretical Chemistry – Biomineralization, ‘https://www.chemie.uni-konstanz.de/ag-peter/research/research-projects/material-science-related-topics/biomineralization/’

2. Papers
2-1. Properties and applications of halloysite nanotubes: recent research advances and future prospects, Peng Yuan a,d,□, Daoyong Tan b, Faïza Annabi-Bergaya, Applied Clay Science, 2015
2-2. Thermodynamics of Proton Binding of Halloysite Nanotubes, Clemente Bretti,† Salvatore Cataldo,‡ Antonio Gianguzza,‡ Gabriele Lando,† Giuseppe Lazzara,‡Alberto Pettignano,*,‡ and Silvio Sammartano†, J of Physical Chem. 2016
2-3. An assembly of organic-inorganic composites using halloysite clay nanotubes, Giuseppe Lazzara a,□□, Giuseppe Cavallaro a, Abhishek Panchal b, Rawil Fakhrullinc, Anna Stavitskaya d, Vladimir Vinokurov d,□□, Yuri Lvovb,d,□, Current Opinion in Colloide interface science, 2017

3. Books
3-1. Soil and Water Chemistry: An Integrative Approach, Second Edition, Av Michael E. Essington, p86

4. Work from Constanza Tedesco
4-1. Powerpoint Presentation ‘Halloysite Presentation’, 2018