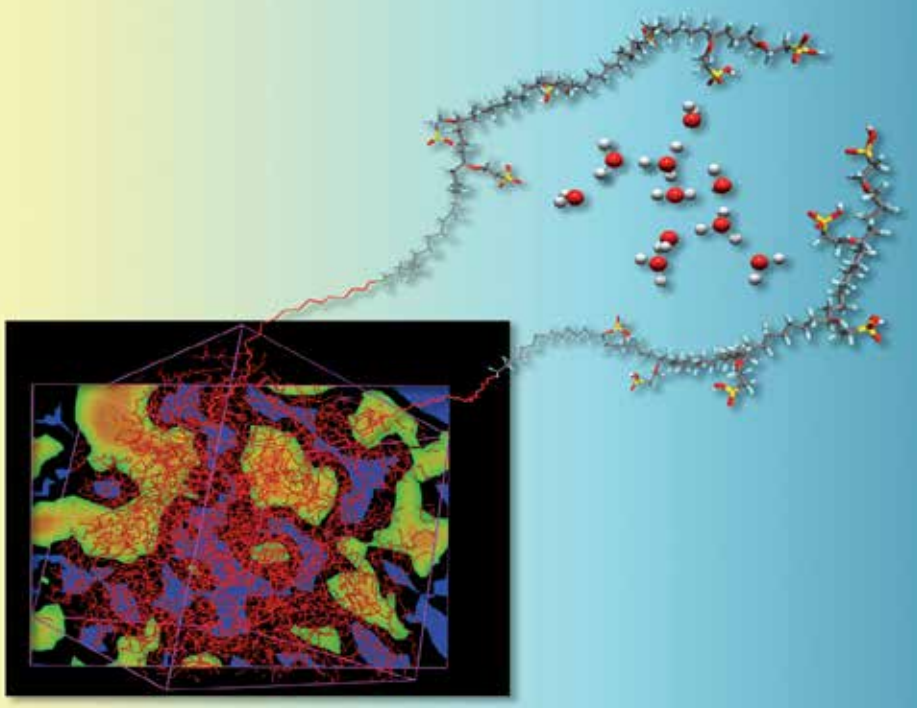
Computer Simulation of Advanced Materials

Lomonosov Moscow State University

Multiscale modelling in Materials Science



James Elliott

(Джеймс Эллиотт)

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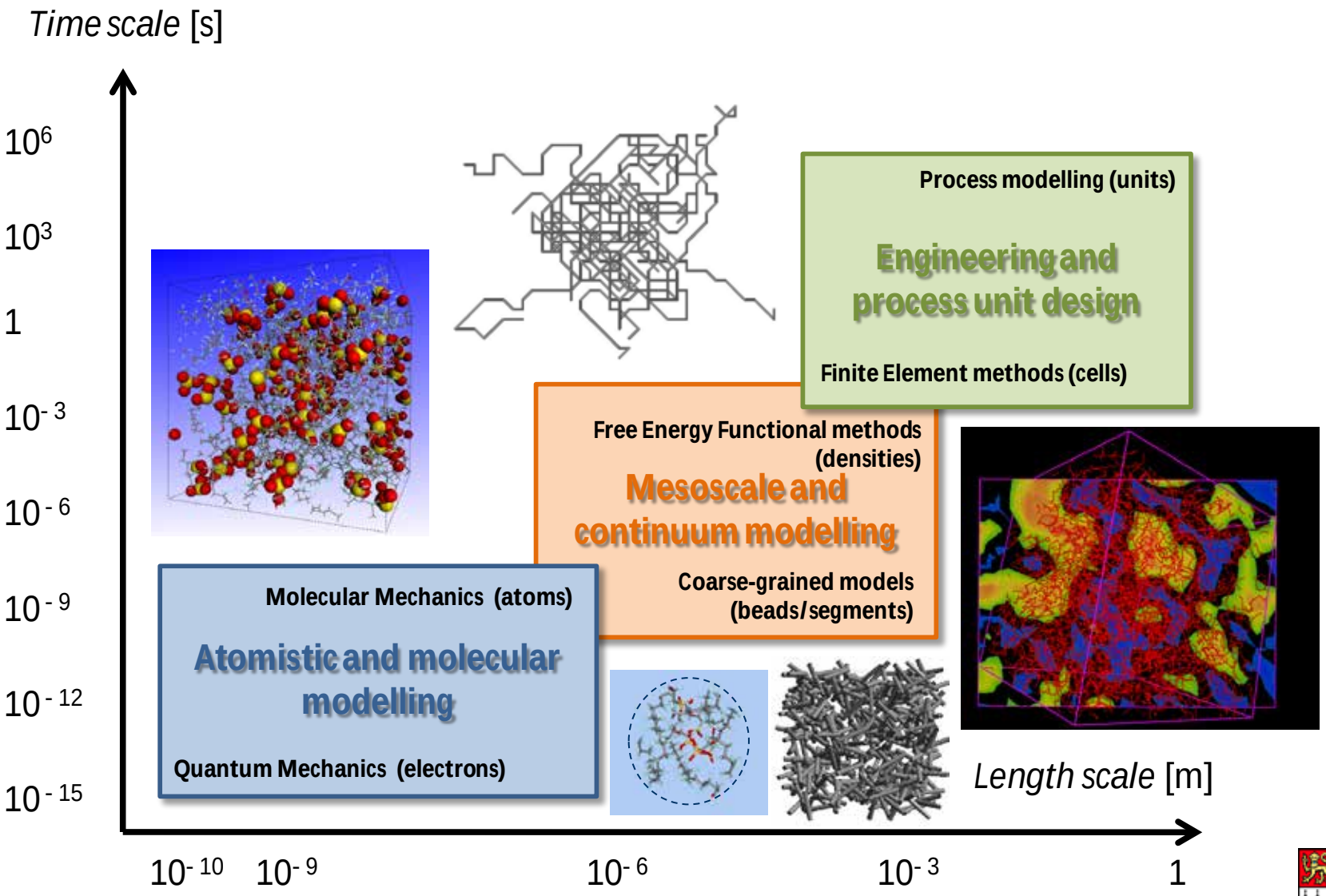
http://www.elliotts.org.uk

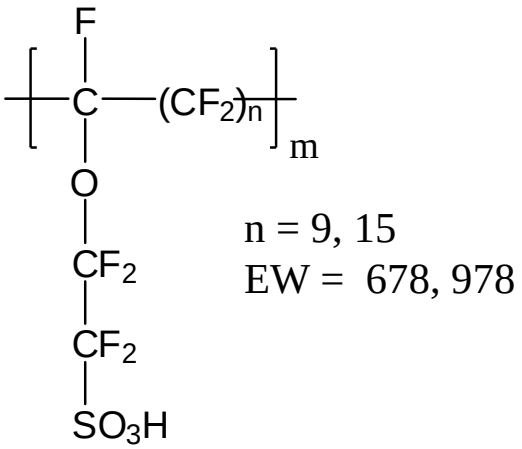
Multiscale Hierarchy for Materials Modelling



J. A. Elliott "Novel Approaches to Multiscale Modelling in Materials Science" *Int. Mat. Rev.* (2011).

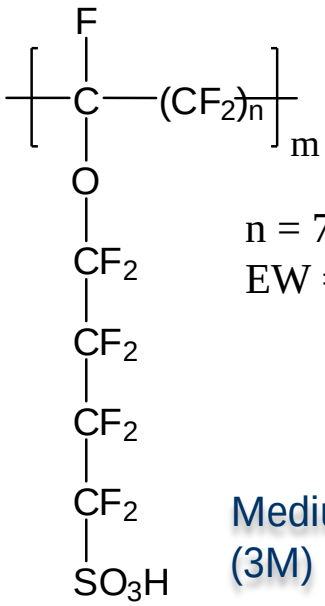
Polymer electrolyte membranes for fuel cells

- Structural family of **P**er**F**luoro**S**ulphonic **A**cid (PFSA) ionomers



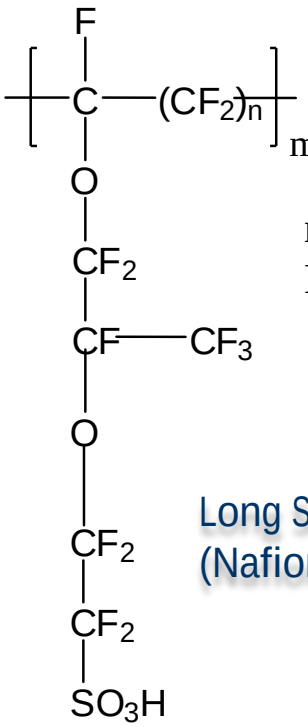
n = 9, 15
EW = 678, 978

Short Side Chain (SSC, Dow, Aquavion)



n = 7, 13
EW = 678, 978

Medium Side Chain (3M)

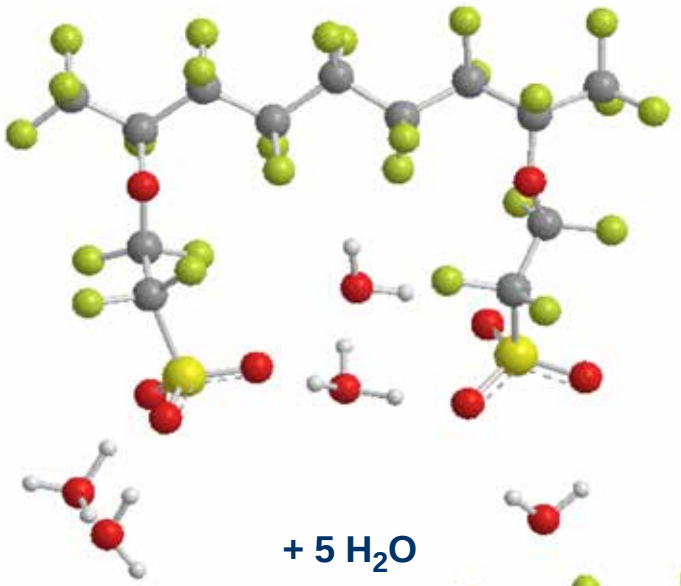


n = 17
EW = 1244

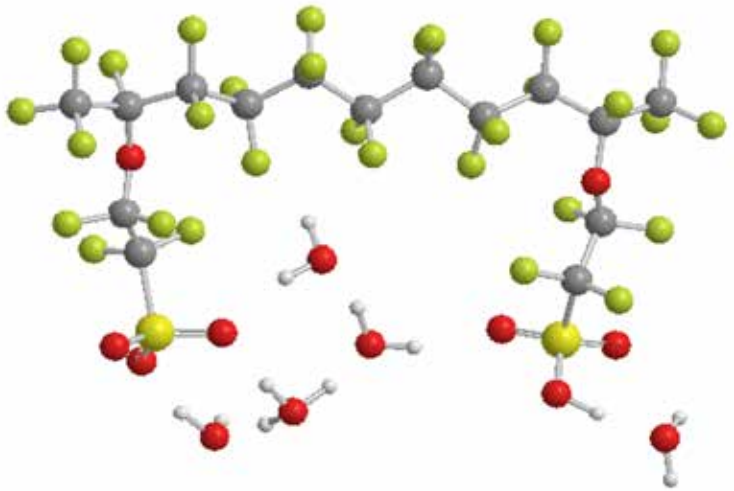
Long Side Chain (Nafion)

- Differ only by the *length* and *distribution* of side chains
- How do differences in chemical structure affect the material and functional properties of membrane?

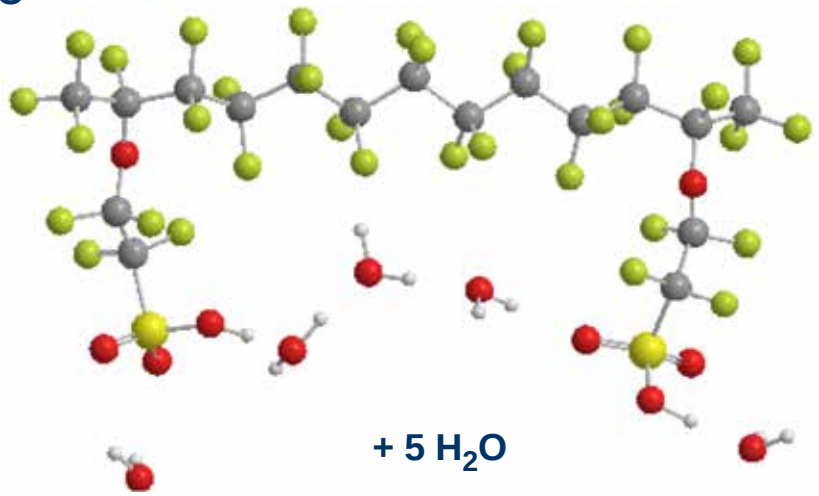
Proton *dissociation* vs. side chain separation



+ 5 H_2O



+ 5 H_2O



+ 5 H_2O

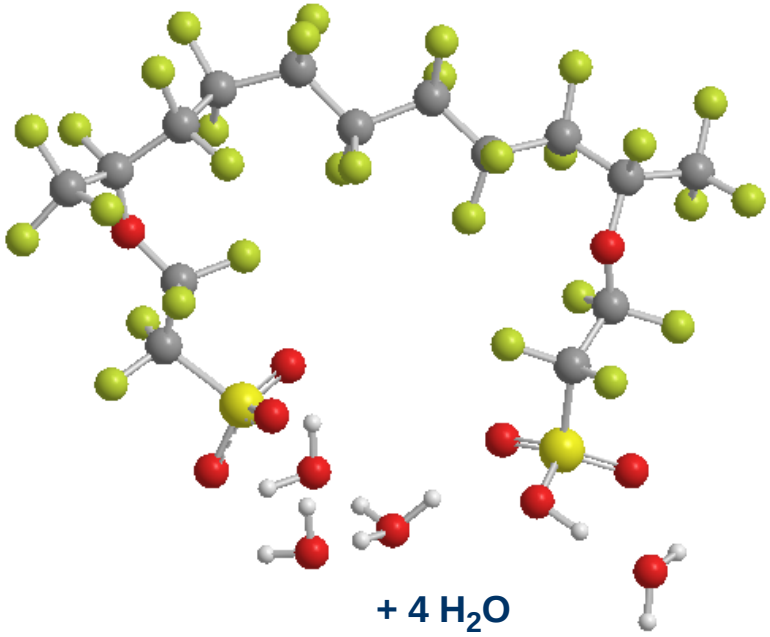
B3LYP/6-311G**

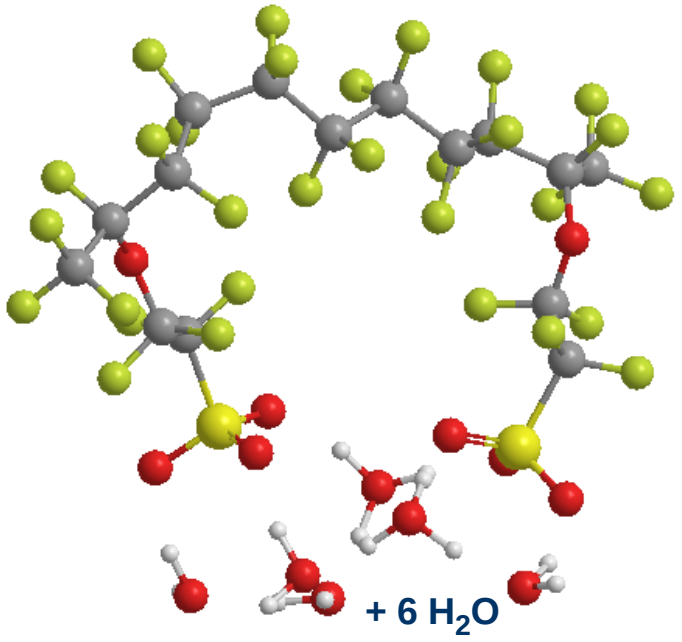
[1] S.J. Paddison and J.A. Elliott, *J. Phys. Chem. A* **109**, 7583-7593 (2005)

Proton *dissociation* vs. water content

$CF_3CF(–O(CF_2)_2SO_3H)–(CF_2)_7–CF(–O(CF_2)_2SO_3H)CF_3$

$+ ? H_2O$





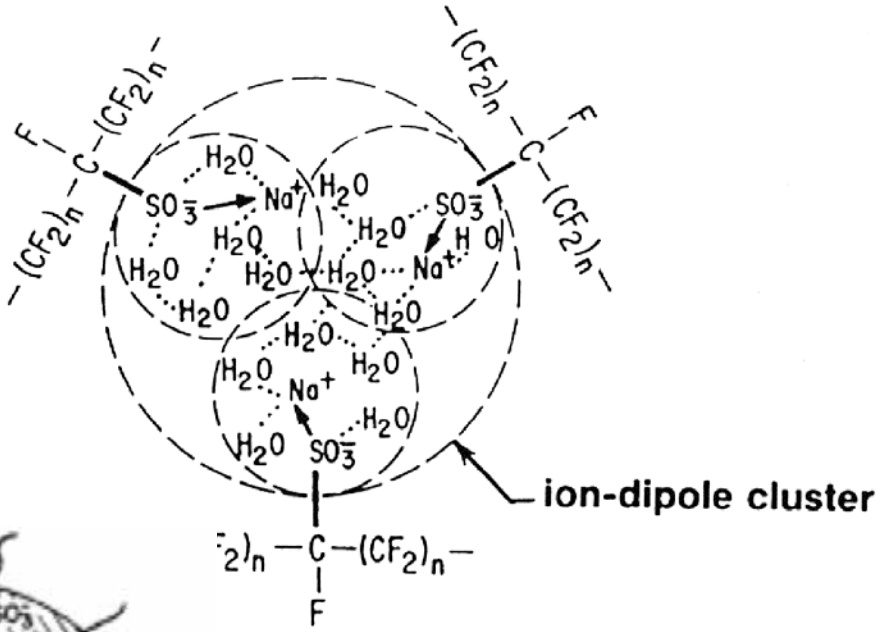
B3LYP/6-311G**

[1] Paddison SJ & Elliott JA, *Phys. Chem. Chem. Phys.* **8**, 2193-2203 (2006)

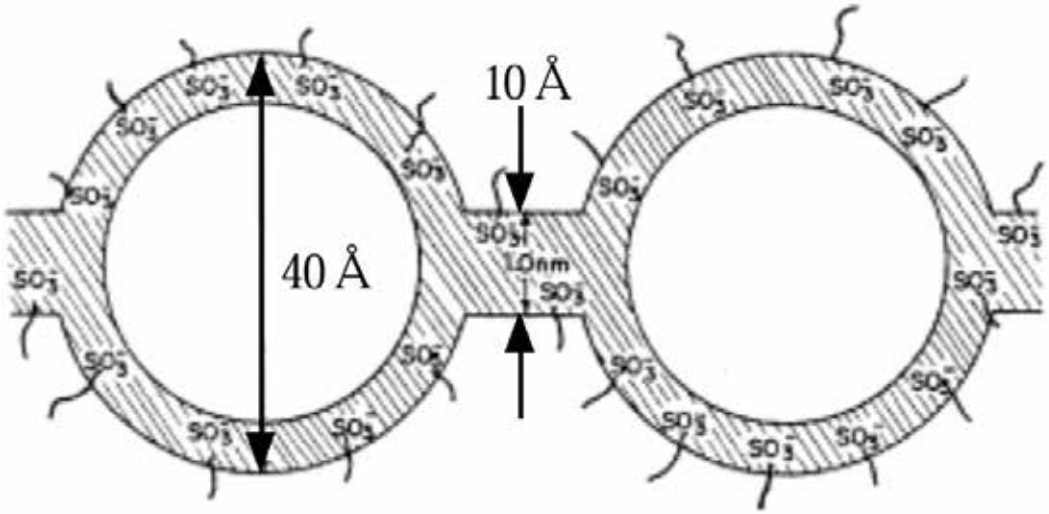
[2] Paddison SJ & Elliott JA, *Solid State Ionics* **177**, 2385-2390 (2006).

Early models for aggregation in ionomers

- Multiplet & cluster model [1]

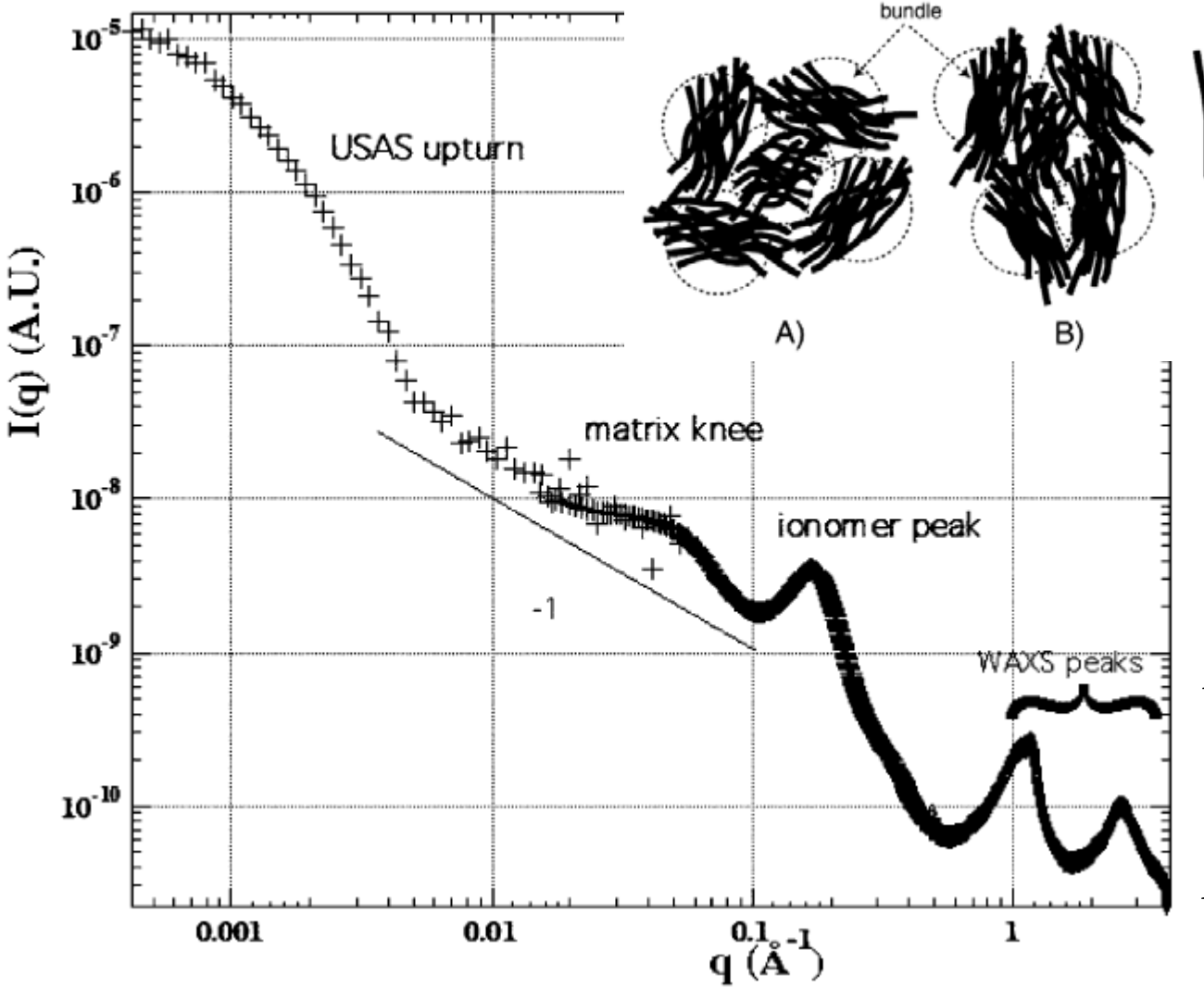


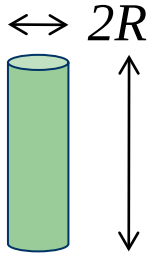
- Cluster-network model [2]



[1] Mauritz, KA, Hora, CJ & Hopfinger, AJ *Ions in polymers* Adv. Chem. Series No. 187 (1980)
[2] Hsu, WY & Gierke, TD *J. Membrane Sci.* **13**, 307-326 (1983)

Fibrillar model of Grenoble group (Diat, Gebel)





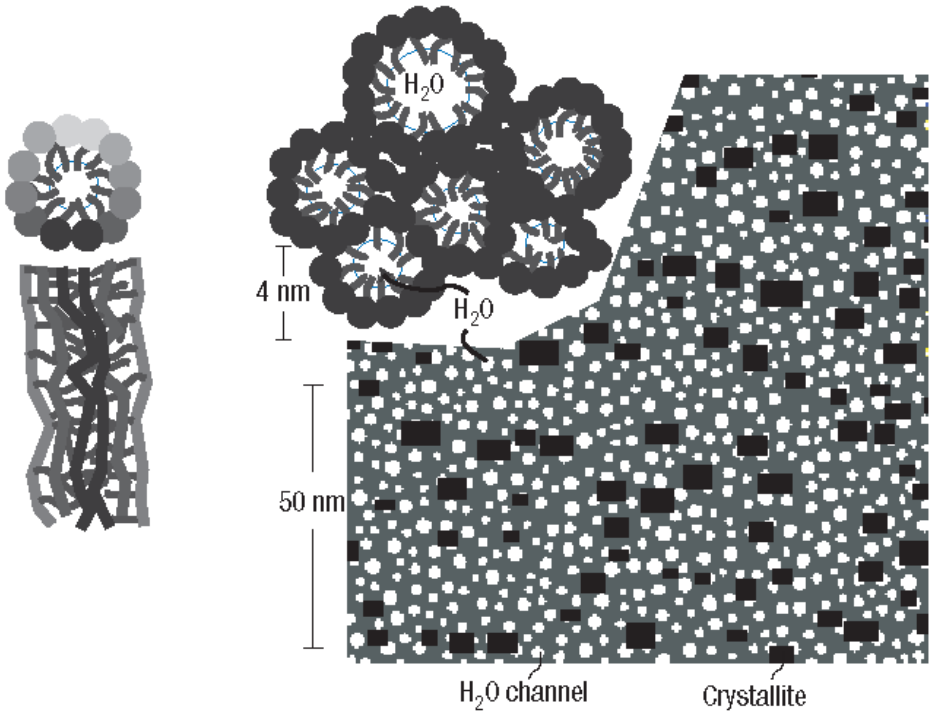
$$I(q) \sim \frac{\exp(-q^2R^2/4)}{qL}$$

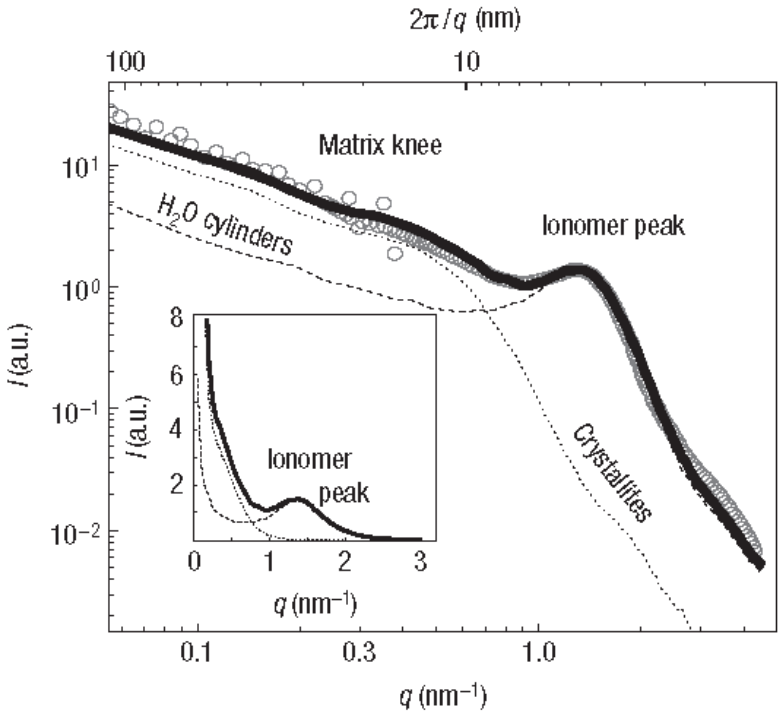
$\Rightarrow q^{-1}$ for small q

R @3 nm, $L \geq 100$ nm

[1] Rubatat L, Rollet AL, Gebel G & Diat O *Macromolecules* **35**, 4050-4055 (2002).
[2] van der Heijden, PC, Rubatat, L & Diat, O *Macromolecules* **37**, 5327-5336 (2004)

Parallel cylinder model of Schmidt-Rohr

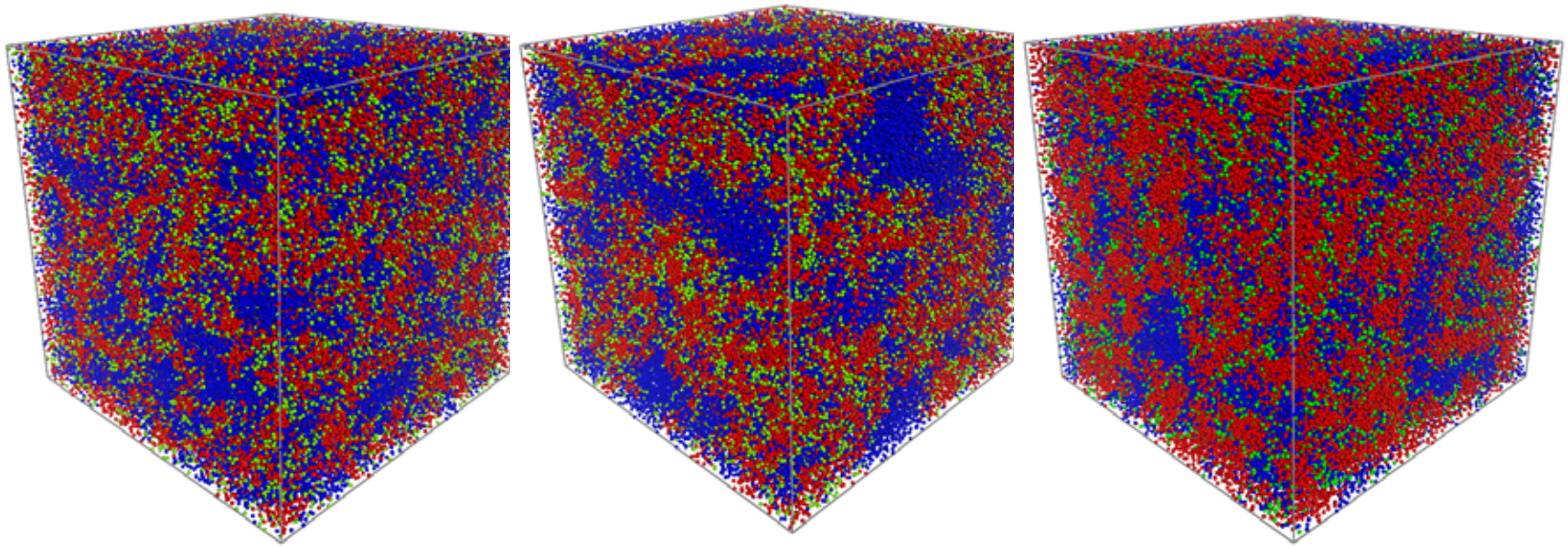




- Cylindrical water-filled channels (white) and crystallites (black) (L > 100 nm) running perpendicular to the plane of slide
- Scattering profile calculated numerically (via FFT) from 2D charge distribution before being averaged in 1D

Schmidt-Rohr K & Chen Q *Nature Materials* **7**, 75–83 (2008)

Simulating PFSA morphology using DPD

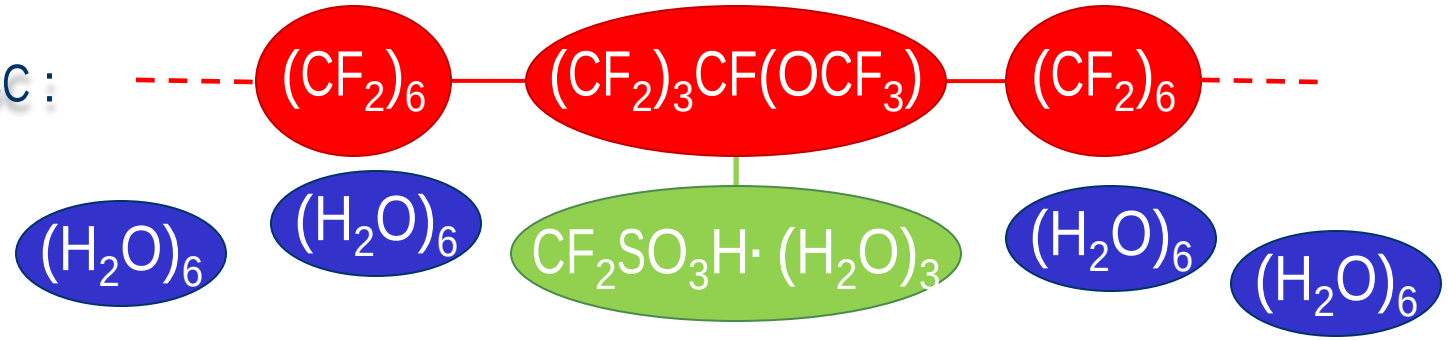


Short Side Chain (SSC)
EW = 678, l = 16

Medium Side Chain (3M)
EW = 678, l = 16

Long Side Chain (Nafion)
EW = 1244, l = 16

For SSC :



Wu D, Paddison SJ & Elliott JA, *Energy Environ. Sci.* **1**, 284–293 (2008)

DPD parameterization procedure

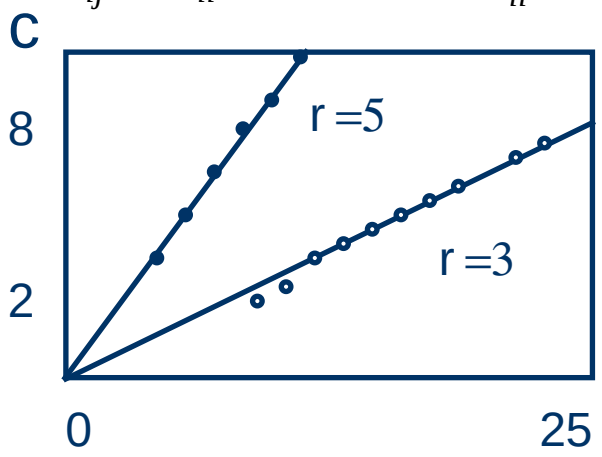
- Each bead acted on by pairwise sum of forces over neighbours

$$\mathbf{f}_i = \sum_{j \neq i} (\mathbf{F}_{ij}^{C} + \mathbf{F}_{ij}^{D} + \mathbf{F}_{ij}^{R} + \mathbf{F}_{ij}^{S}).$$

$$\mathbf{F}_{ij}^{S} = -C(r_0 - r_{ij})\mathbf{n}_{ij}$$

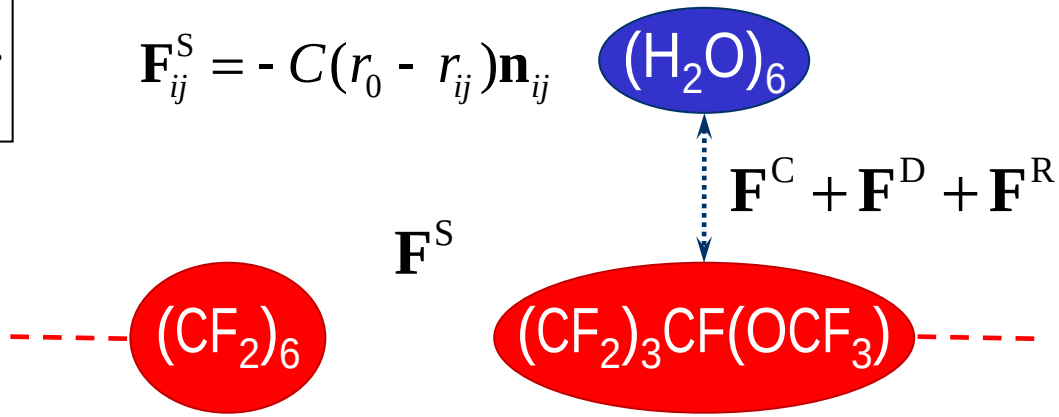
$$\mathbf{F}_{ij}^{C} = \begin{cases} -a_{ij}(r_c - r_{ij})\mathbf{n}_{ij} & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases}$$

$$a_{ij} = a_{ii} + 3.27\chi \qquad a_{ii} = 25 k_B T$$



[1]

$$\frac{a_{ij} - a_{ii}}{k_B T}$$



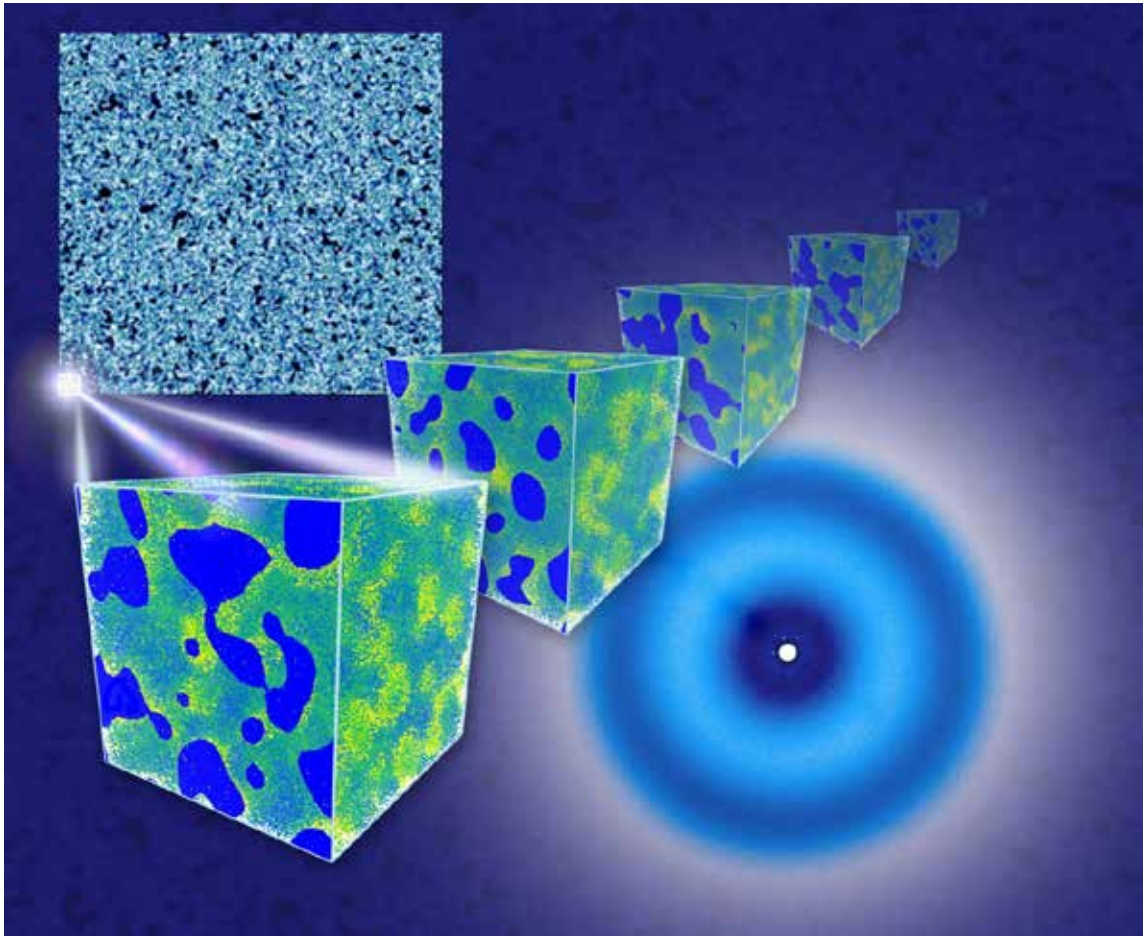
[2]

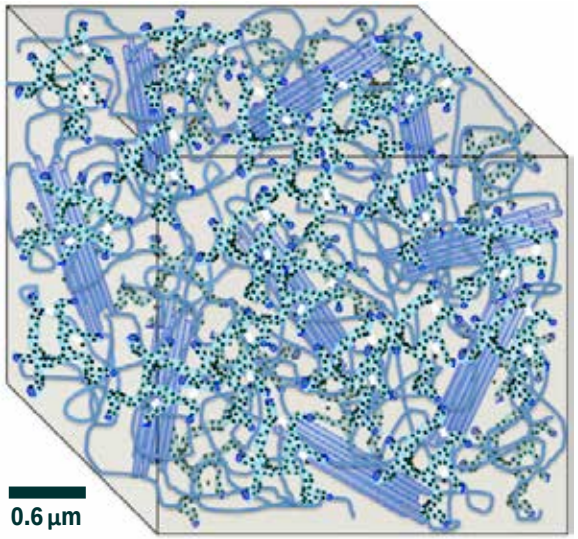
Pair[a]	χ	a_{ij} (k_BT)
A–*B*	0.15	25.5
A–*C*	6.86	47.4
A–*W*	3.28	35.7
B–*C*	6.24	45.4
B–*W*	3.15	35.3
C–*W*	1.24	29.0

[a] *A*, $-[CF_2]_6-$; *B*, $-[CF_2]_3CF(OCF_3)-$; *C*, $CF_3SO_3H{\cdot}3H_2O$; and *W*, $6H_2O$.

[1] Groot RD & Warren PB, *J. Chem. Phys.* **107** 4423-4435 (1997).
[2] Wu D, Paddison SJ & Elliott JA, *Energy Environ. Sci.* **1**, 284–293 (2008).

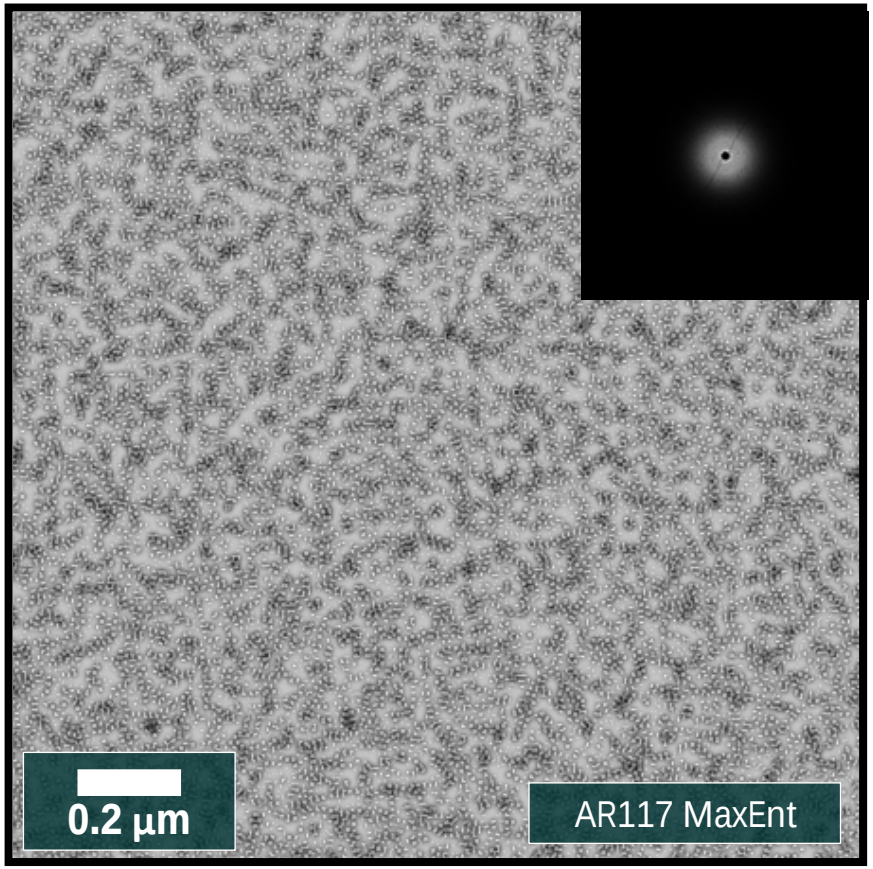
Unified morphology from DPD and SAXS models

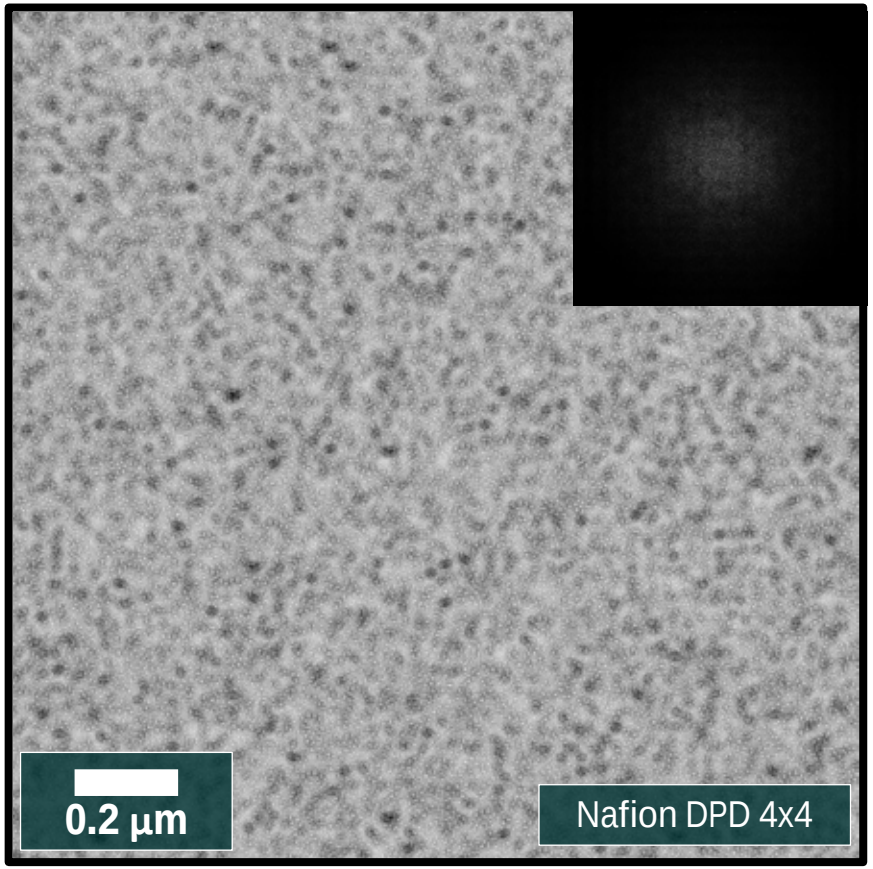




Elliott JA, Wu D, Paddison SJ & Moore RB, *Soft Matter* **7**, 6820-6827 (2011)

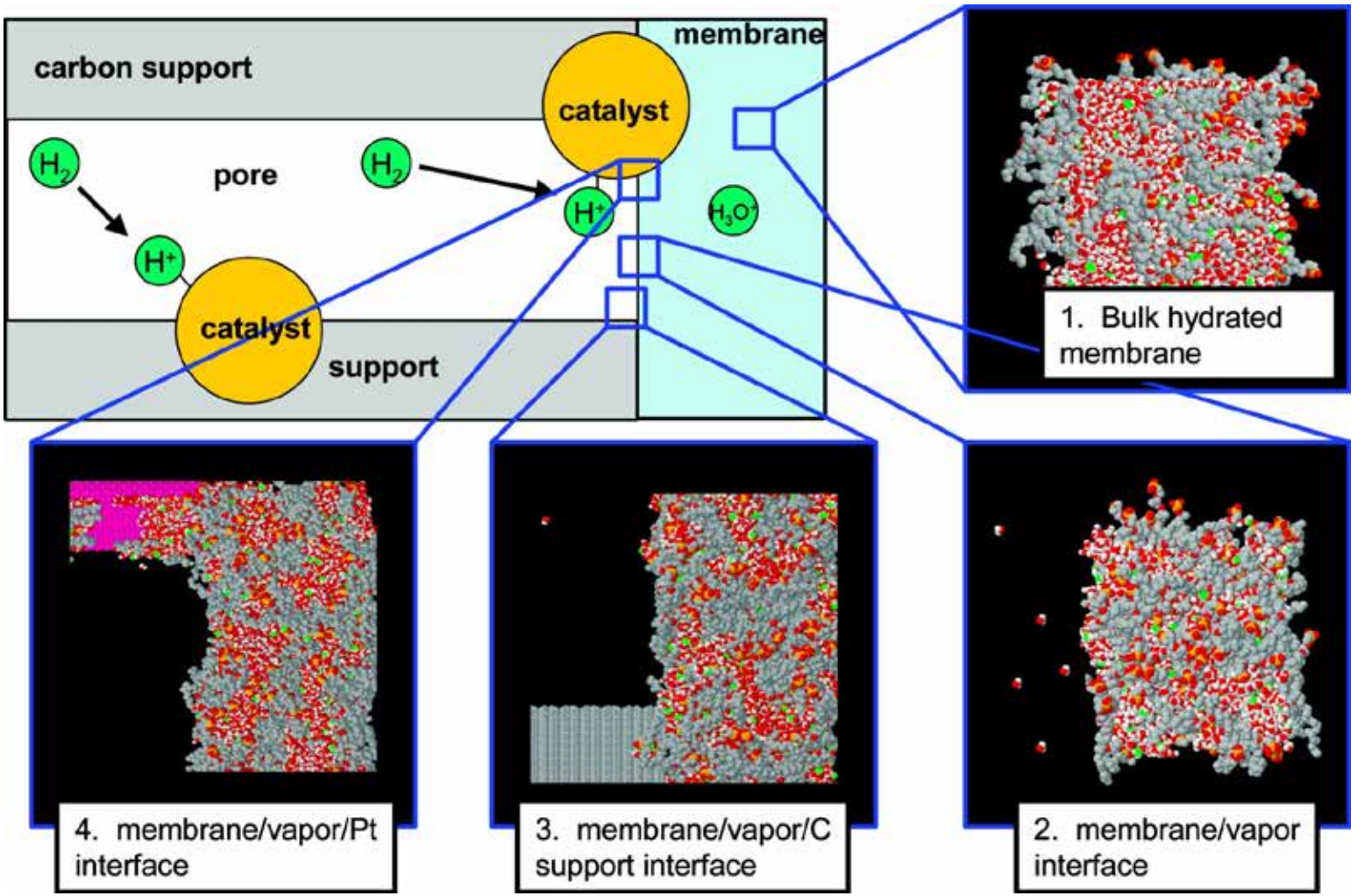
Comparison of 2D SAXS data from MaxEnt and DPD





Elliott JA, Wu D, Paddison SJ & Moore RB, *Soft Matter* **7**, 6820-6827 (2011)

Electrode/electrolyte interfaces at PEM cell anode

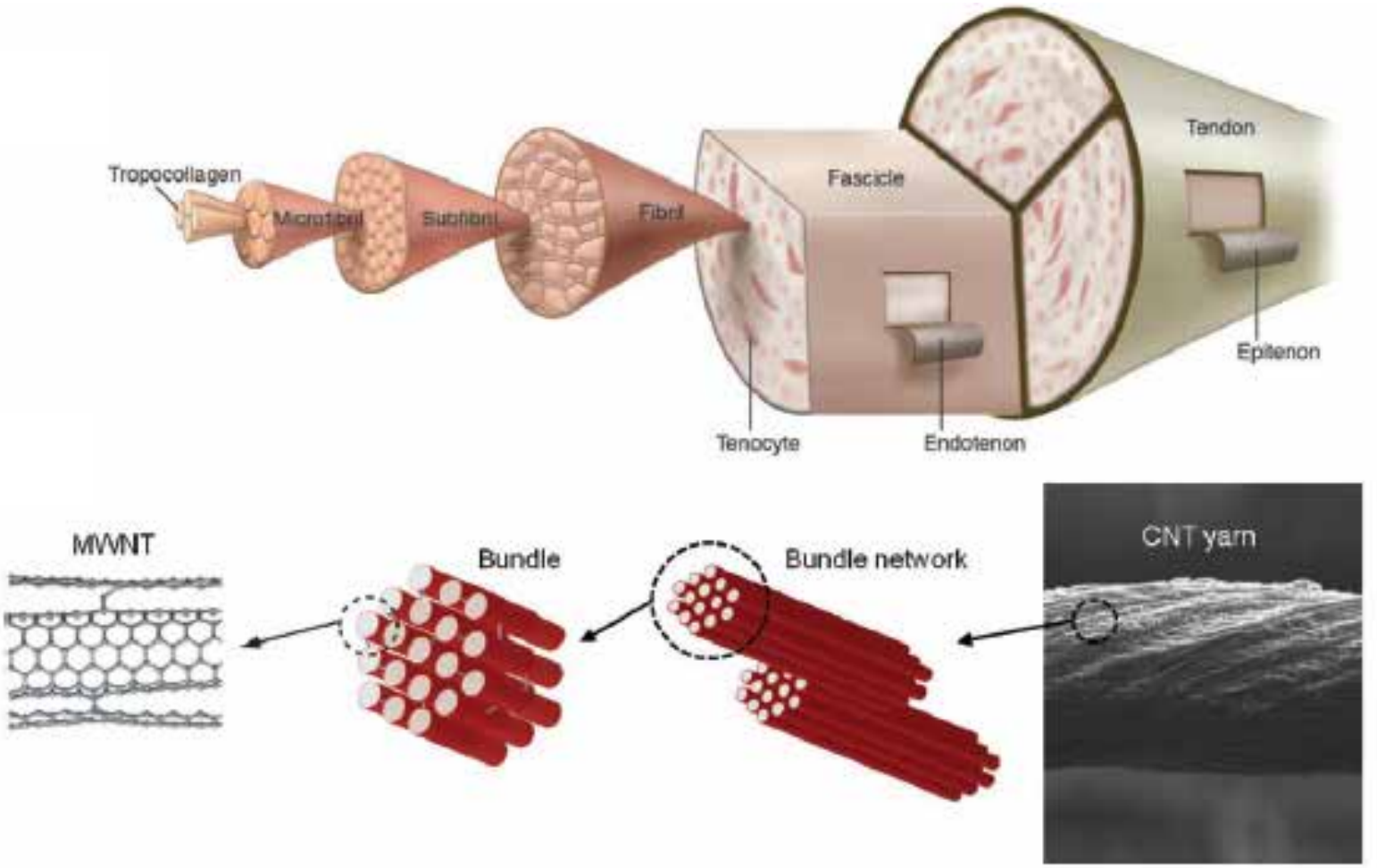


[1] Liu; Selvan; Cui; Edwards; Keffer; Steele; *J. Phys. Chem. C* **112** 1985-1993 (2008).

Summary of nanocomposite morphology

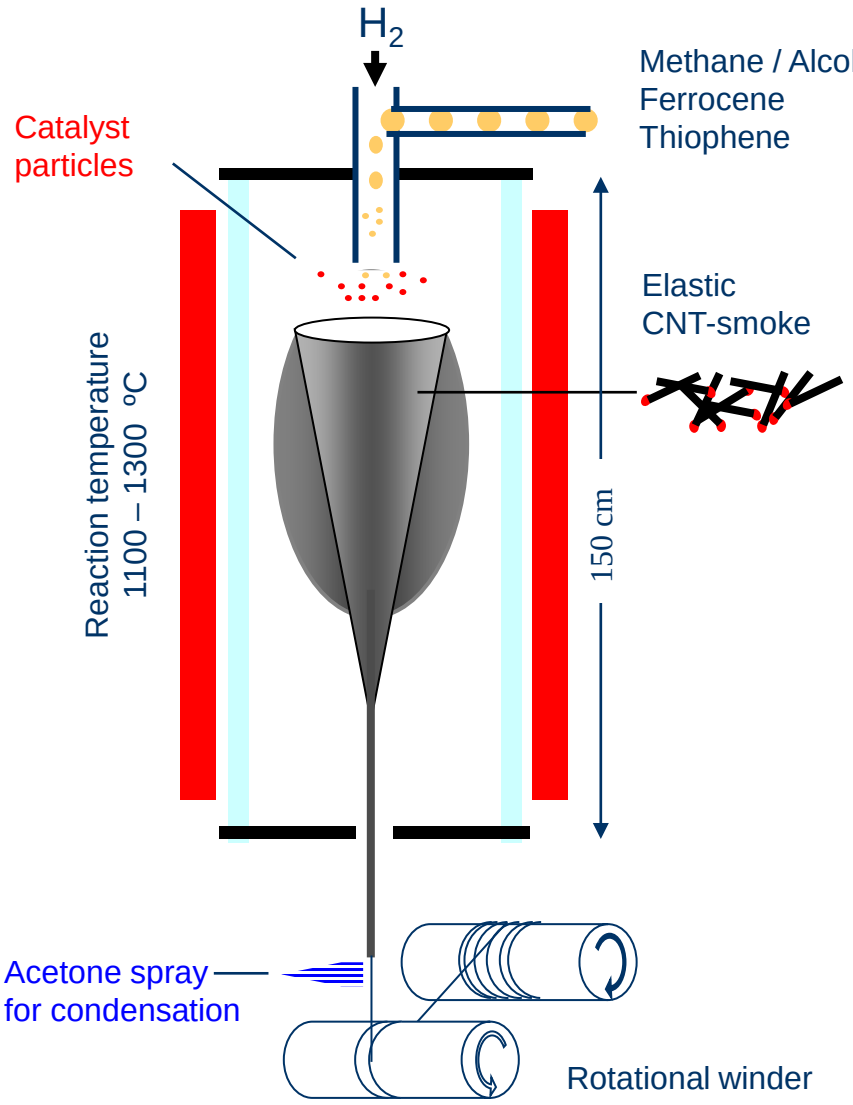
- Confinement of polymeric phase into *2D slab* with nanoscopic width, *L*, gives rise to *discrete layers of water channels*
- When *L* = 5 nm (approximately 'cluster' size for bulk membrane), obtain just *singe channel*, bordered by side chains
- In case of GO, with more hydrophilic surface than graphene, more water seen close to interface for smallest layer (5 nm)
- When *L* > 10 nm, channel swells and begins to split into multiple channels. No significant difference between graphene and GO at interface
- Side groups strongly adsorb to Pt even though "non-adsorbing"
- Existence of discrete channels of ionic aggregates, frustrated due to confinement by pores in catalyst support

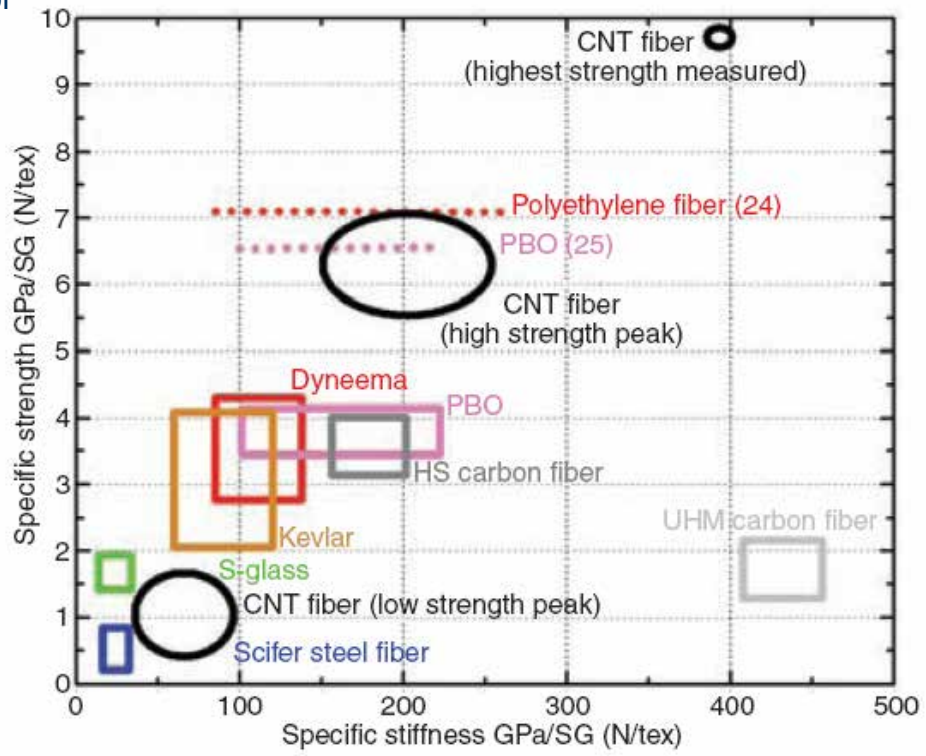
Multiscale structure of hierarchical nanomaterials



[1] Espinosa, Filleter and Naraghi *Adv. Mater.*, **24**, 2805 (2012).

CVD-grown nanotube fibres with high specific strength

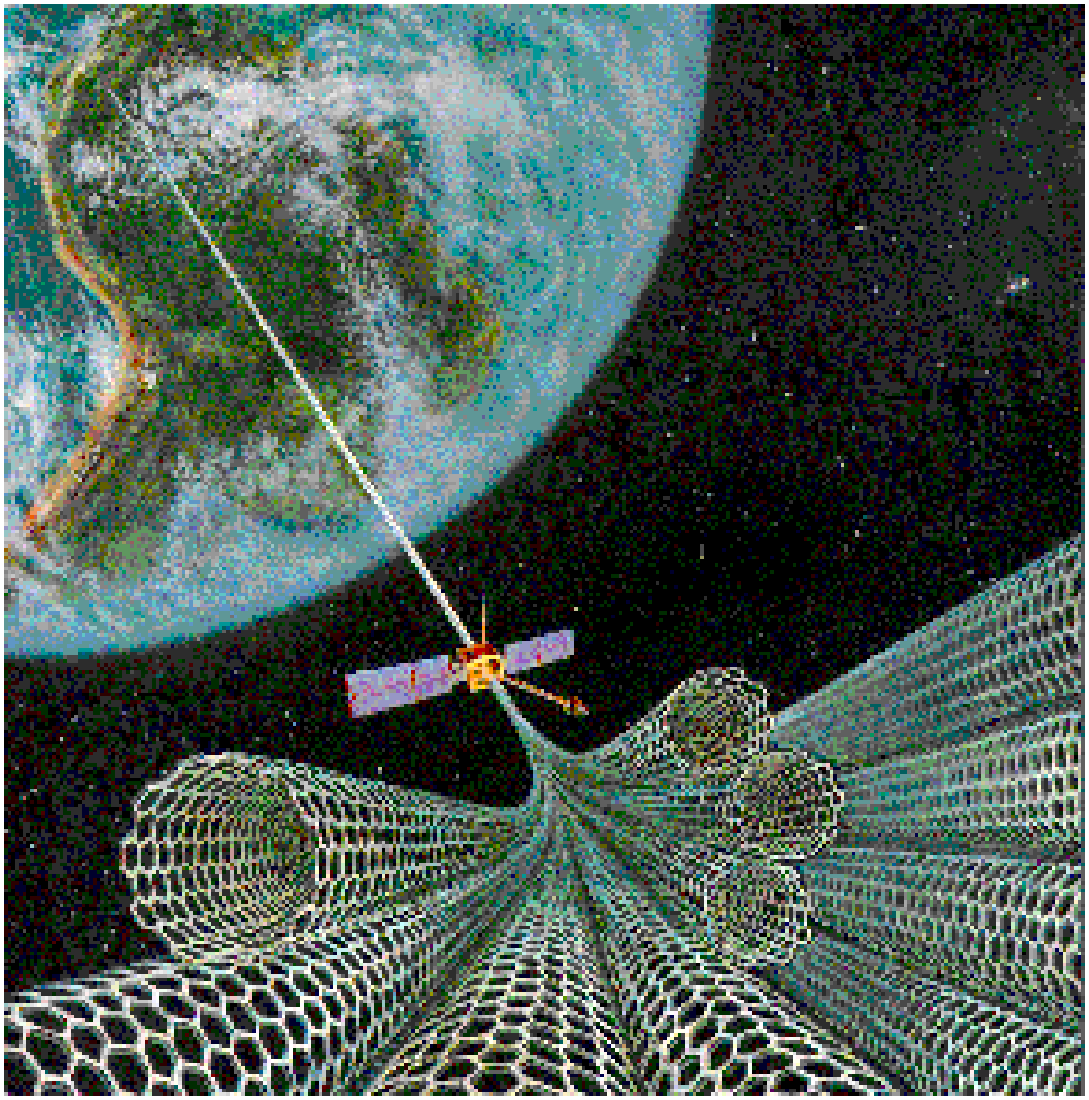




$$\frac{N}{tex} = \frac{GPa}{SG} \qquad SG = \frac{r_{fibre}}{r_{water}}$$

[1] Motta, et al. *Advanced Materials*, **19**, 3721-3726 (2007).
[2] Koziol et al., *Science*, **318**, 1892-1895 (2007).

A material strong enough for a “space elevator”?



$E = 1\ \text{TPa}$

$\sigma_f = 120\ \text{GPa}$

?

[1] B. I.Yakobson and R .E.Smalley, *American Scientist* **85**, 324-337 (1997).

Macroscopic model for CNT bundle strength [1]

- Assembly of ‘short’ fibrous elements which fail in shear at a specific strength, s’, given by:

$$s\text{¢} = \frac{1}{6} W_1 W_2 t_F L \quad \text{[N/tex]}$$

W_1 is **ratio of** nanotubes on the **perimeter of the bundle to the total** number of tubes (SWCNT = 1, DWCNT » 0.5, fibre < 0.1)

W_2 is **proportion of** a nanotubes in **contact with neighbours** (estimated » 0.85 for fibres from both experimental TEM and atomistic simulations)

t_F is the **shear strength** between graphene layers (assumed 50 kPa)

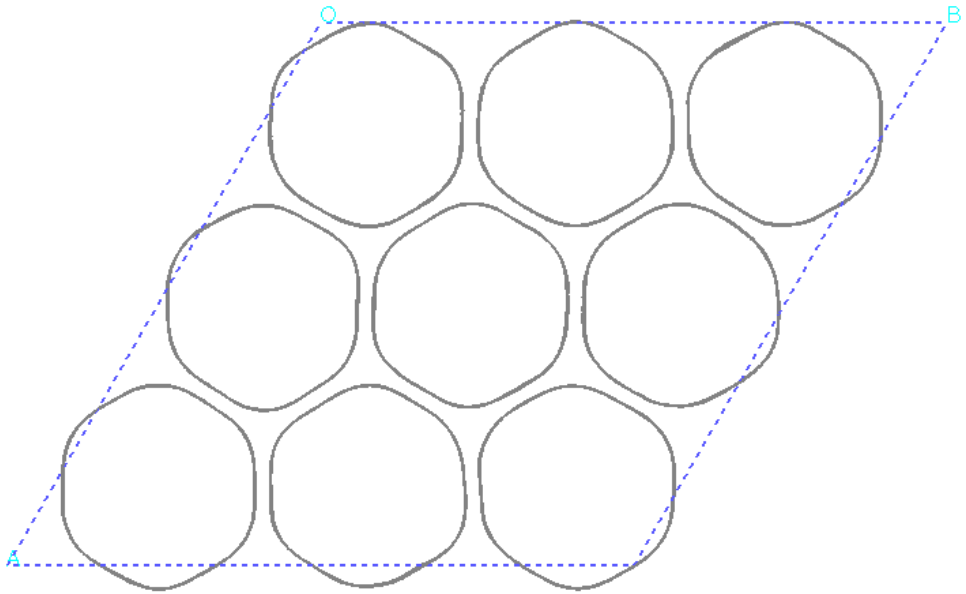
L is the **length of fibrous elements** (» 1 mm, aspect ratio 10^5)

- Using these values, obtain a tensile strength of 3.54 N/tex

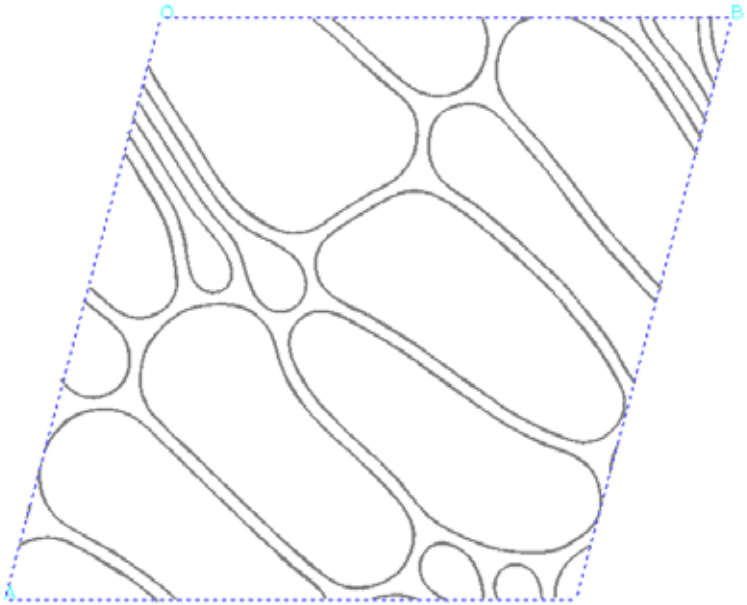
[1] Vilatela, Elliott and Windle, *ACS Nano* **5** 1921-1927 (2011).

Effect of tube collapse/polygonization on W_2

- Limit to stability of larger tubes at ambient pressure Þ spontaneous collapse due to tube polygonization & flattening



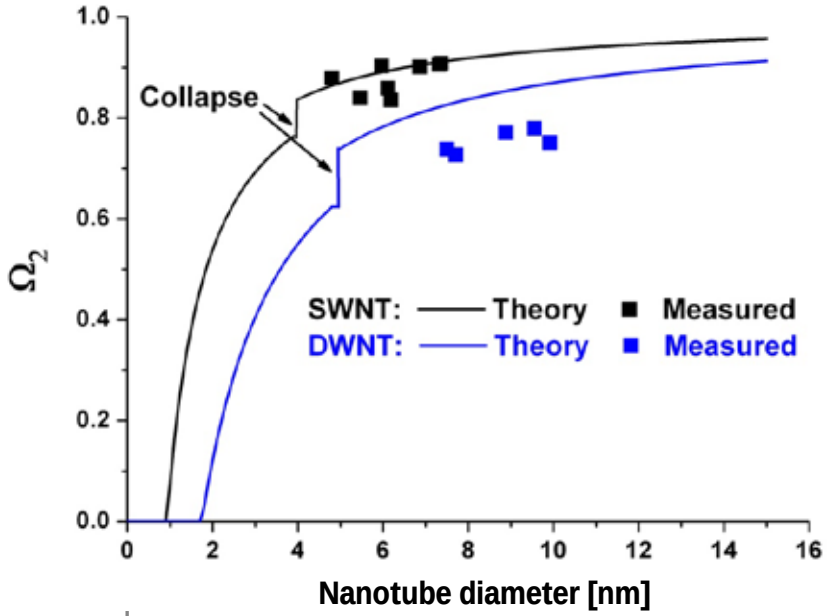
(30,30) SWNT
diameter 4.16 nm

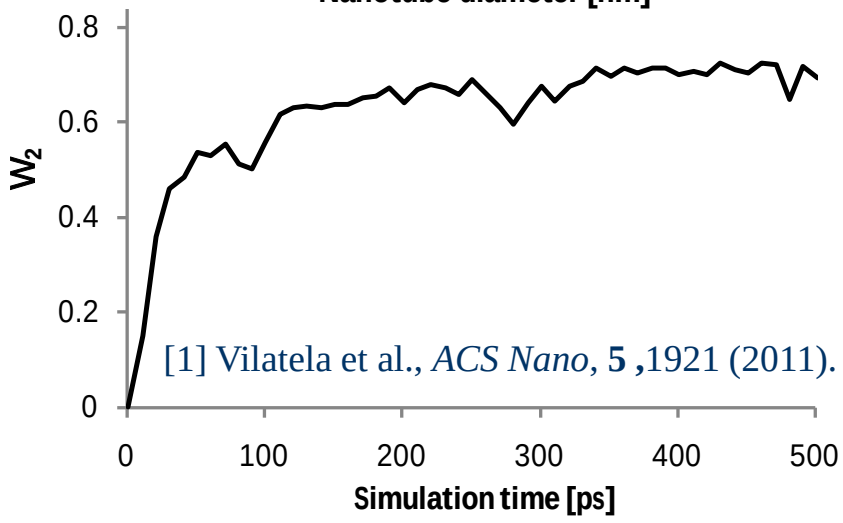


(50,50) SWNT
diameter 6.94 nm

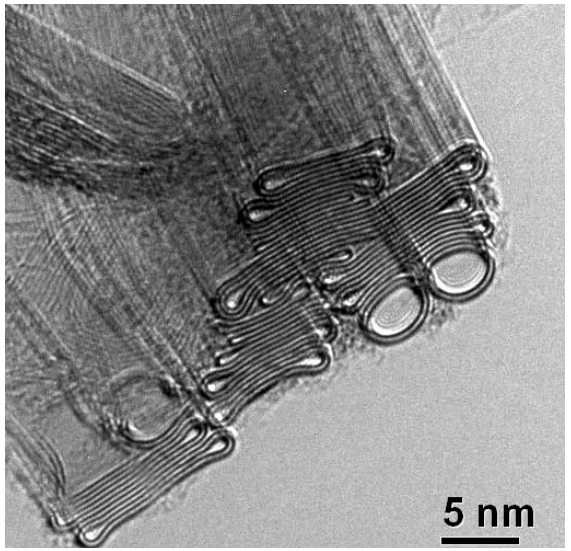
[1] Elliott et al., *Phys. Rev. Lett.*, **92**, 095501 (2004).

Effect of tube collapse & polygonization on W_2

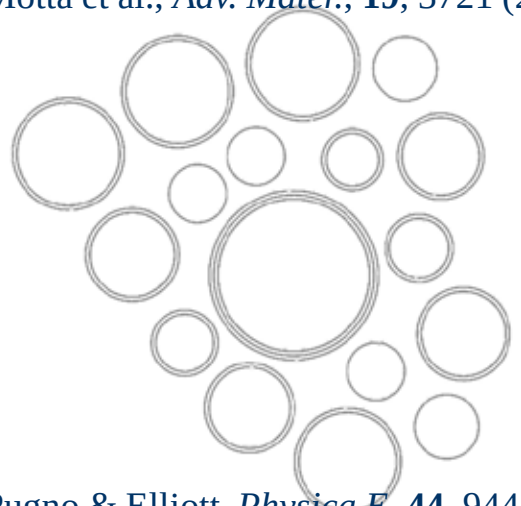




[1] Vilatela et al., *ACS Nano*, **5** ,1921 (2011).



[2] Motta et al., *Adv. Mater.*, **19**, 3721 (2007).



[3] Pugno & Elliott, *Physica E*, **44**, 944 (2012).

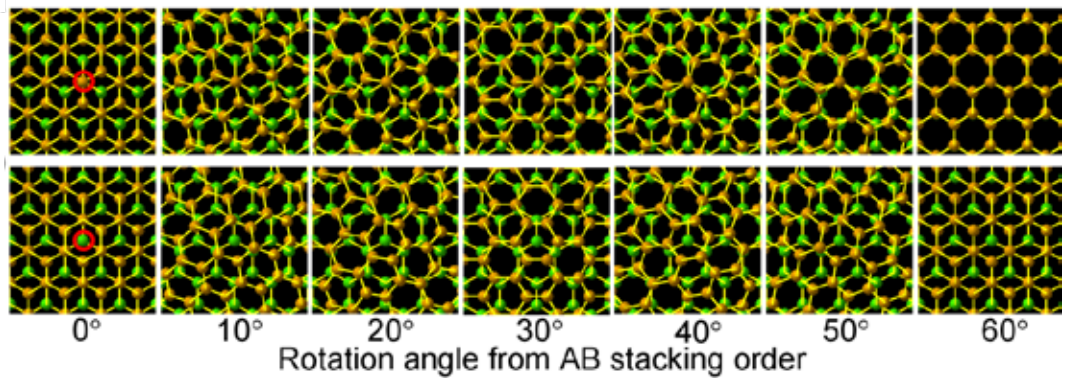
Range of wall/sheet shear strength, t_F

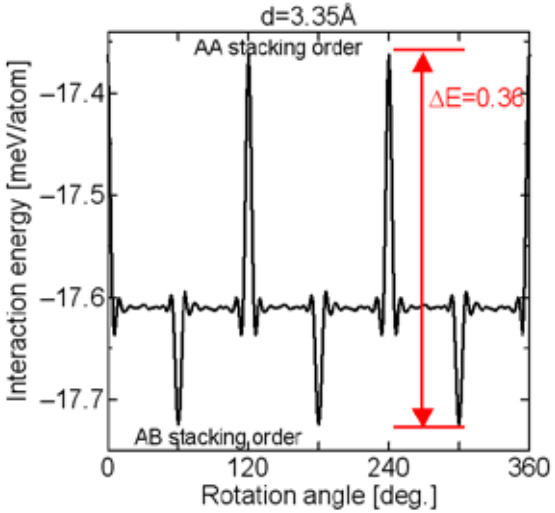
- Wide range of measured strengths: from 0.04 to 69.0 MPa.

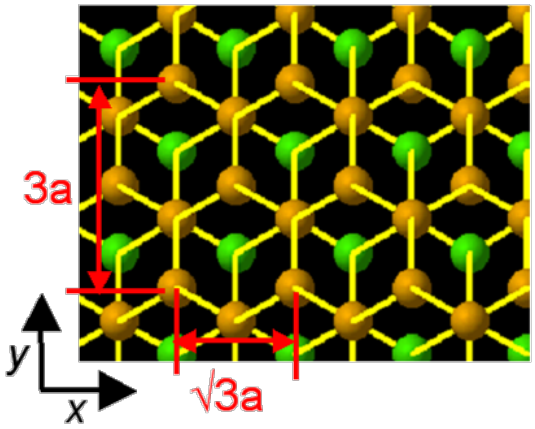
Material	Method	Shear strength (MPa)	Reference
Single crystal Graphite	Mechanical shear	0.029	[1]
MWNT on Graphite	Tube rolling and sliding	2.0	[2]
MWNTs	Intratube sliding	0.08	[3]
MWNTs	Intratube sliding	>0.04	[4]
SWNTs/ MWNTs	Intratube sliding	4.0	[5]
MWNTs	Intratube sliding	2.0 – 69.0	[6]

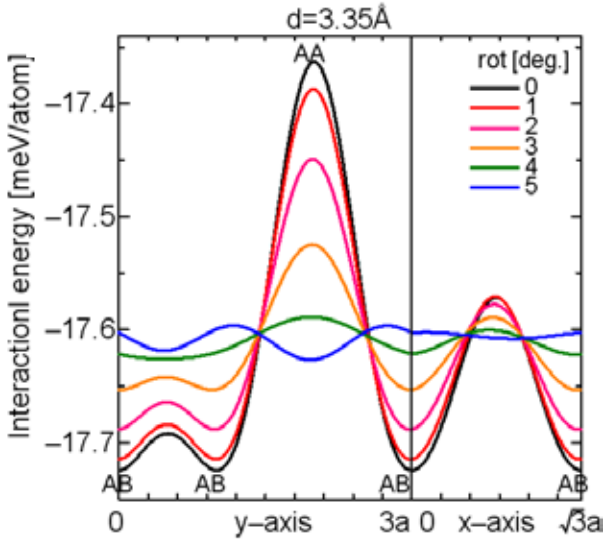
[1] Soule, D. E. & Nezbeda, C. W. *J. App. Phys.* **39**, 5122-5129 (1968).
[2] Falvo, M. R. *et al.*, *Nature* **397**, 236-238 (1999).
[3] Yu, M., Yakobson, B. I. & Ruoff, R. S. *J. Phys. Chem.* **104**, 8764-8767 (2000).
[4] Kis, A., Jensen, K., Aloni, S., Mickelson, W. & Zettl, A. *Phys. Rev. Lett.* **97**, 025501 (2006).
[5] Bhushan, B., Ling, X., Jungen, A. & Hierold, C. *Phys. Rev. B* **77**, 165428 (2008).
[6] Suekane, O., Nagataki, A., Mori, H. & Nakayama, Y., *App. Phys. Exp.* **1**, 064001 (2008).

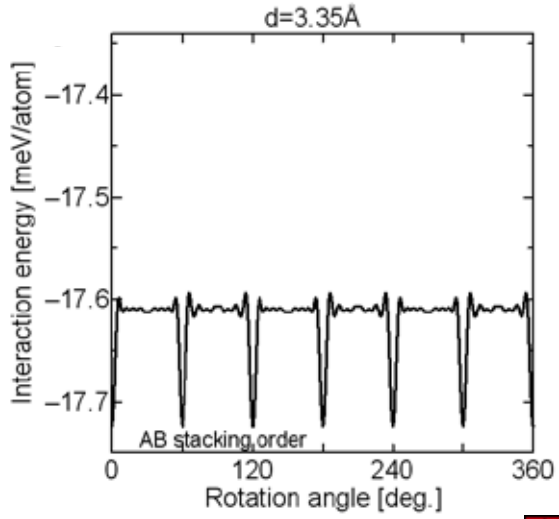
Sliding of turbostratic bilayer graphene is facile











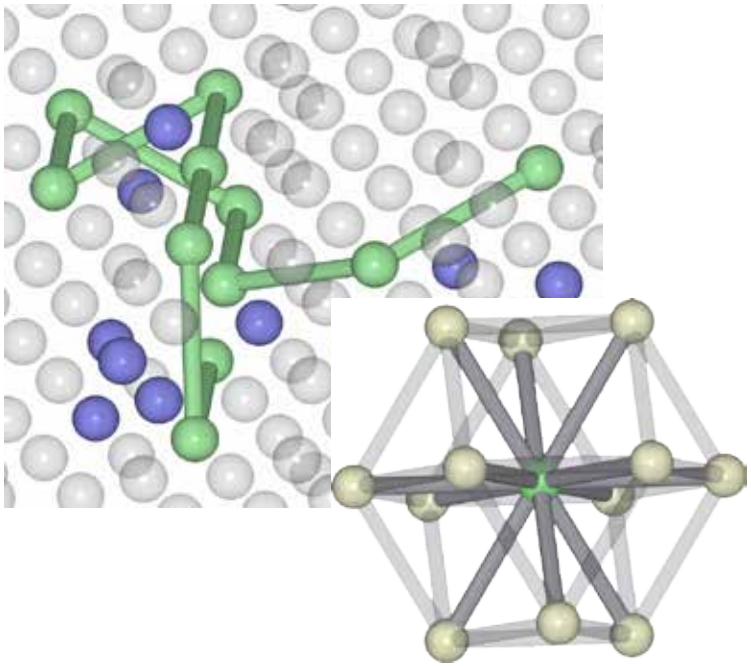
[1] Shibuta and Elliott *Chem. Phys. Lett.*, **512**, 146-150 (2011).

Summary: prospects to increase CNT fibre strength…

- W_1, W_2 : fairly close to limits already (although good idea to minimize bundle size and number of walls in fibrous elements)
- L : increase length of fibrous elements (1 order possible?)
- t_F : can increase by several orders of magnitude by:
  - irradiation (defects, cross-linking)
  - chemical functionalization
  - introducing polymeric additives
- Irradiation effects – has been assumed that improvement is due to cross-linking effect, but could be due to softening of in-plane stiffness by increasing defect density
- Realistic to expect CNT fibres with strengths reproducibly around 10 N/tex over large lengths

Lattice Monte Carlo (MC) polymer model

A single polymer bead is moved at a time to create a new state in MC simulation [1]



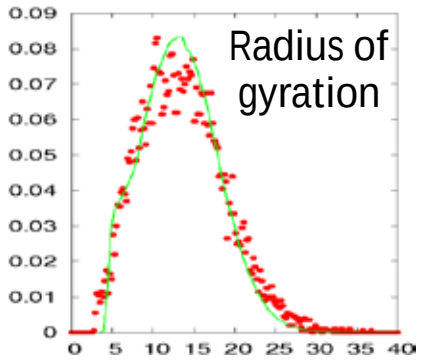
- Standard canonical MC
  - fixed temperature
  - visits states with probability

$$p_{NVT} = D(E)\exp\left(-\beta E\right)$$

- Multicanonical MC [2]
  - visits all energy states with equal probability
  - system statistics at any temperature can be obtained by reweighing

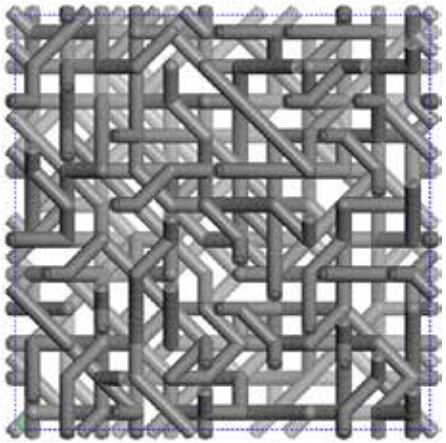
[1] K.R. Haire *et al.*, *Comput. Theor. Polym. Sci.*, **11**, 17 (2001)
[2] F.Wang and D.P. Landau, *Phys. Rev. Lett.*, **86**, 2050 (2001)

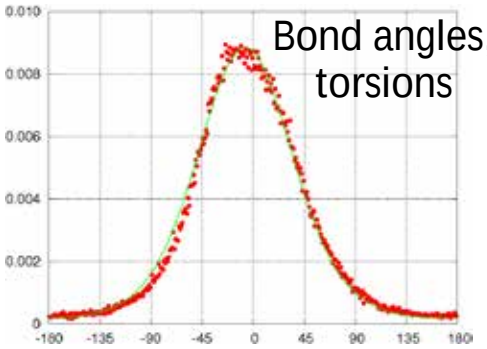
Mapping and reverse-mapping of amorphous PE

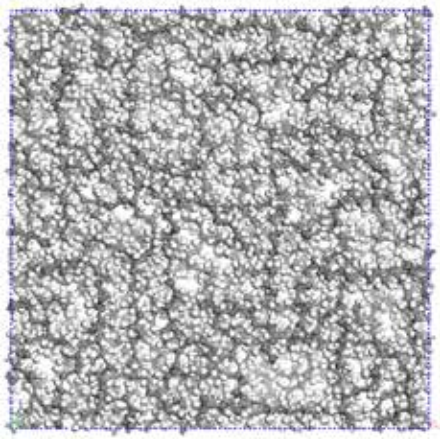


mapping

reverse-mapping (RM)



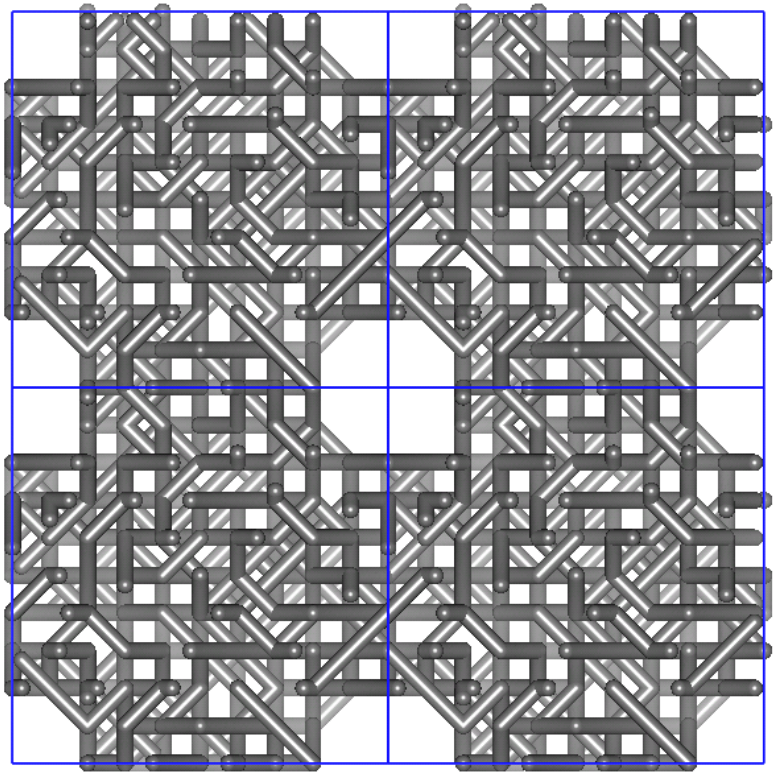


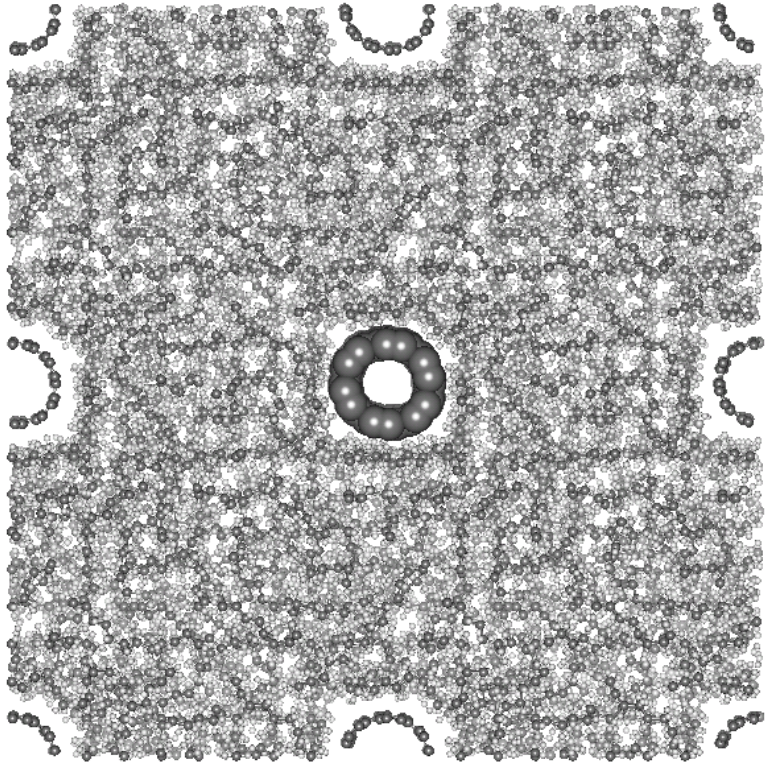


[1] J. Baschnagel et al. *Adv. Polym. Sci.* **152**, 41-156 (2000).
[2] F. Müller-Plathe *ChemPhysChem* **3**, 754-769 (2002).

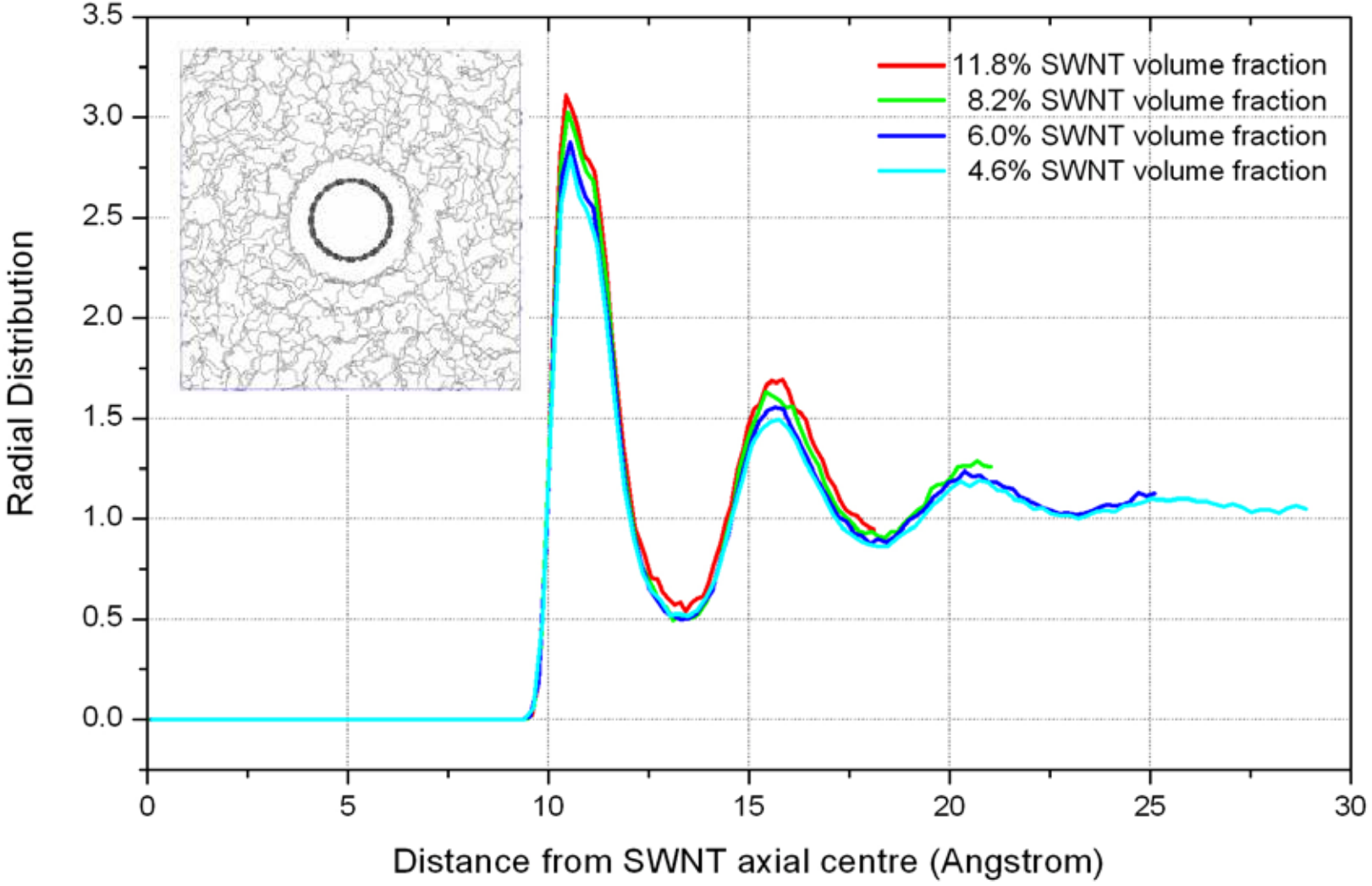
Modelling PE/CNT composite

- 16 chains of PE ($C_{101}H_{204}$) and a (6,6) SWCNT were placed into a periodic cubic cell (f_{CNT} = 0.082)
- System initialized on lattice, and then relaxed atomistically.



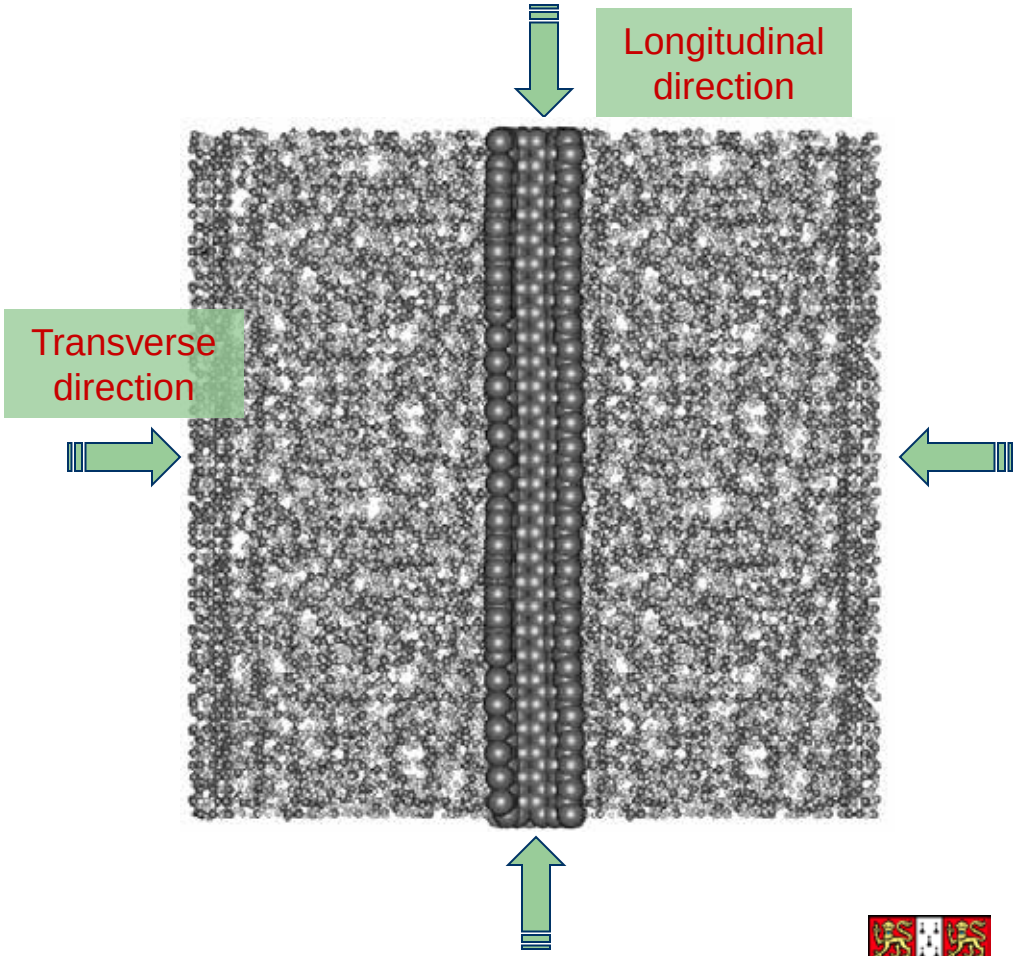


Ordered layering of polymer around SWCNT



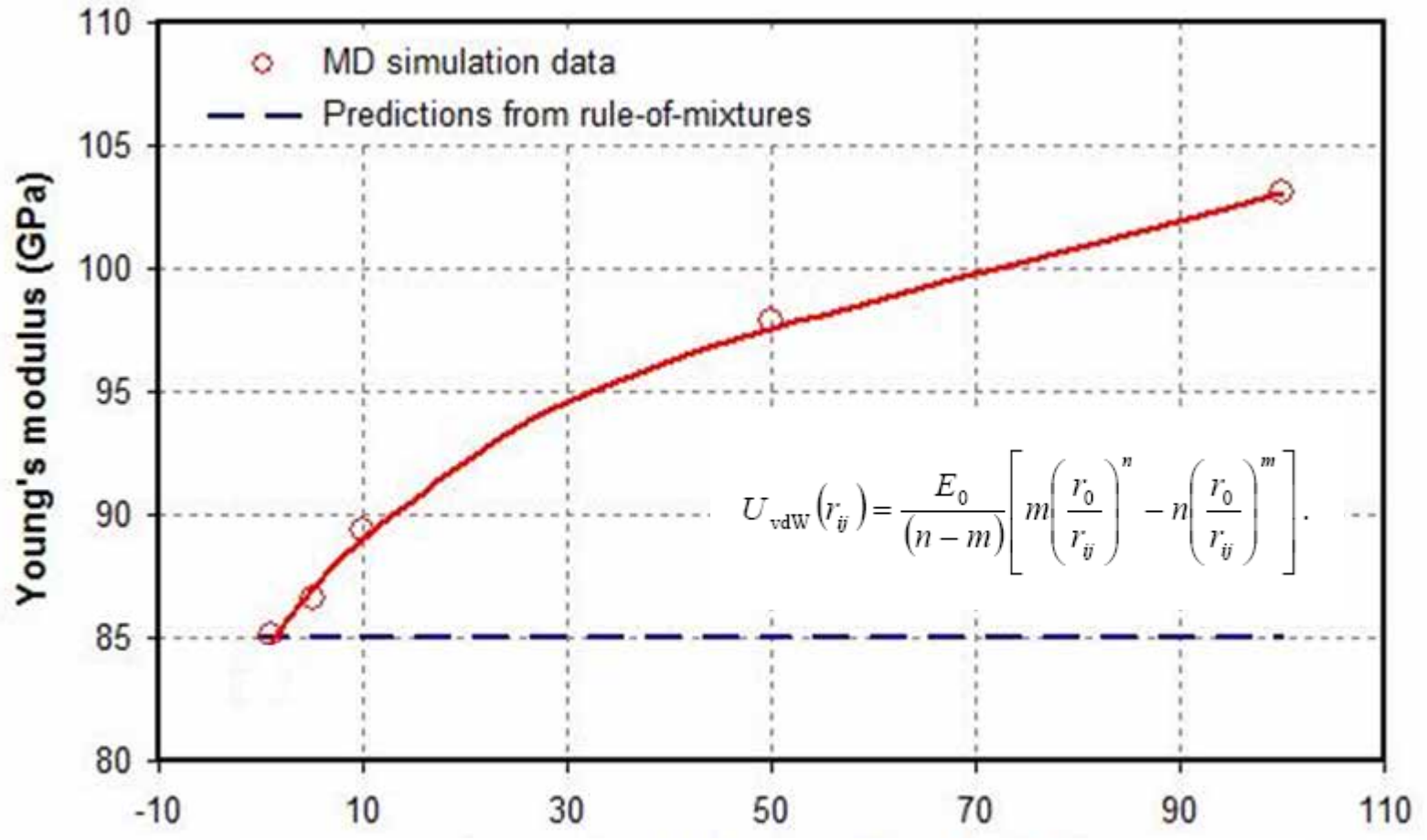
Elastic Properties – Young's Modulus

- Calculation Methodology
  - A stepwise decreasing increment of cell size in longitudinal and transverse directions was applied to the system, separately.
  - A 200 ps NVT run was allowed between each increment for equilibration.
  - The change in stress was measured as a function of the strain.
  - Total strain less than 3% of initial cell size.



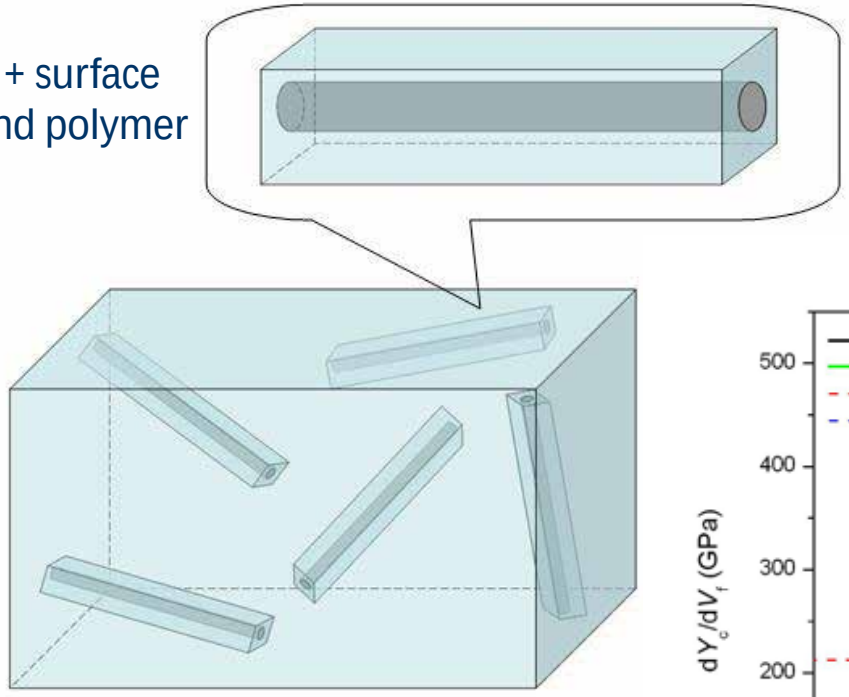
Positive deviation from rule of mixtures

... when interactions between PE-CNT are enhanced

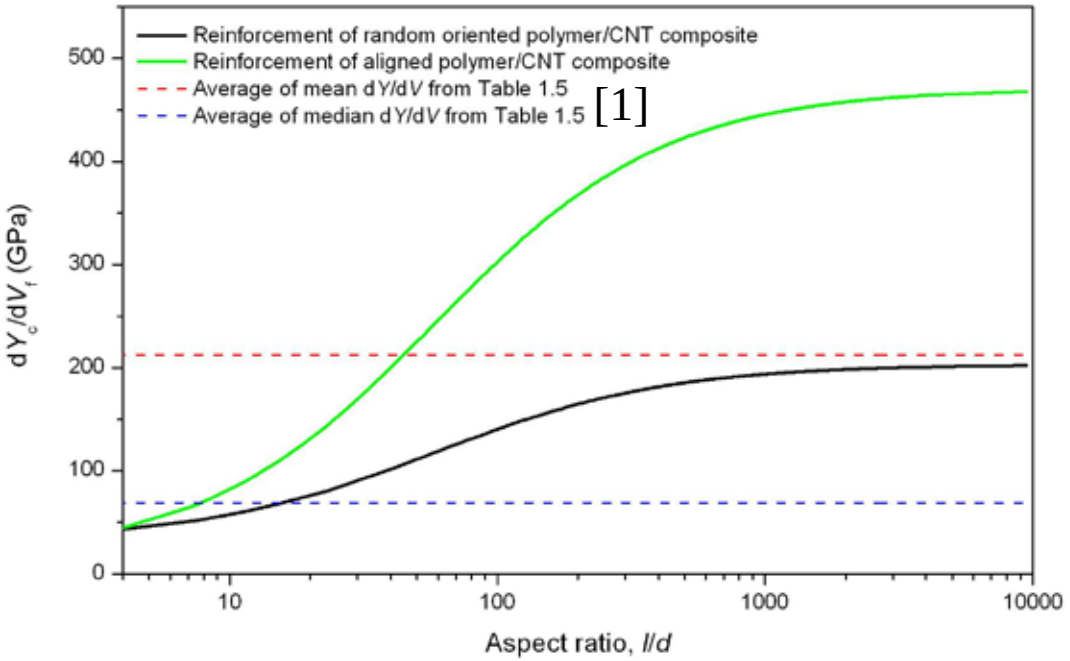


Effective fibre predictions from Halpin-Tsai model

CNT + surface bound polymer



"Effective fibre" axial modulus 85.1 GPa
Perfectly bonded to PE matrix



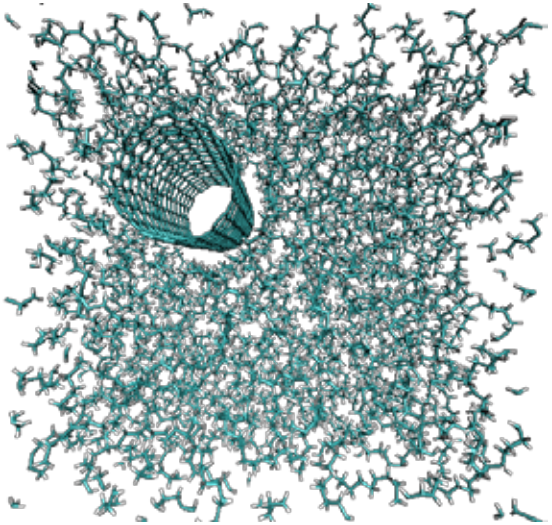
$$\frac{dY_C}{dV_f} \approx Y_m \eta (\zeta + 1) \quad \text{for aligned fibres}$$

$$\frac{dY_C}{dV_f} \approx \frac{3}{8} Y_m \eta_L (\zeta + 1) + \frac{15}{8} Y_m \eta_T \quad \text{for randomly oriented fibres}$$

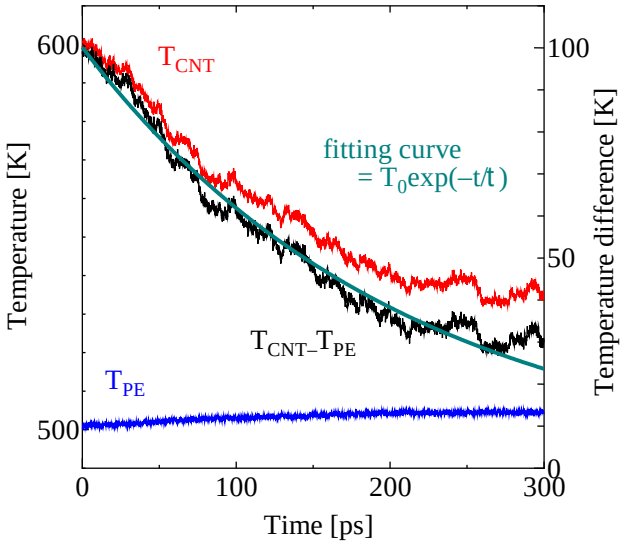
[1] J. N. Coleman, U. Khan, W. J. Blau, and Y. K. Gun'ko, *Carbon* **44**, 1624 (2006).

Interfacial heat transfer between CNT and PE

- System
  - A (10,10) single wall carbon nanotube (CNT) and amorphous polyethylene chains (figure on the right)
- Force field
  - CNT : Universal Force Field[1]
  - Polyethylene : Polymer Consistent Force Field[2]



Lumped heat capacity method[3]



Procedure

Apply heat pulse to the CNT

- Relax the system under microcanonical (NVE) ensemble
- Fit the temperature difference during the relaxation (black line) to the exponential function (green line)

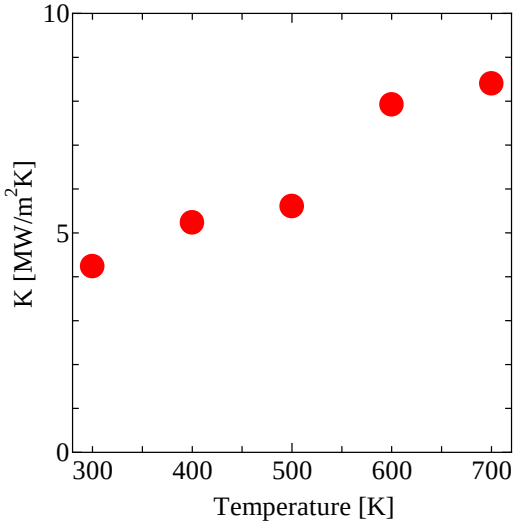
$$K = \frac{1}{\left(\frac{1}{m_{CNT}c_{CNT}} + \frac{1}{m_{PE}c_{PE}}\right) S \cdot t}$$

m : total mass in the system
c : heat capacity
S : interface surface area
t : relaxation time

[1] A. K. Rappe et al. *J. Am. Chem. Soc.* 114, 10024 (1992)
[2] H. Sun et al. *J. Am. Chem. Soc.* 116, 2978 (1994)
[3] C. F. Carlborg et al. *Phys. Rev. B* 78, 205406 (2008)

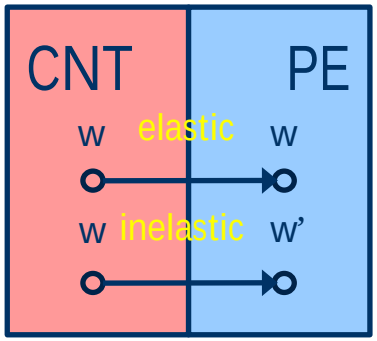
Behaviour of thermal boundary conductance K

Temperature dependence



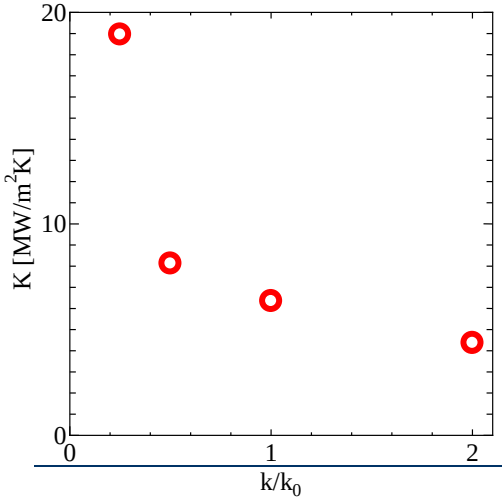
K increases with temperature

Øncrease in inelastic phonon scattering



- Phonon scattering at interface

CNT force constant k dependence (change strength of force field in CNT)

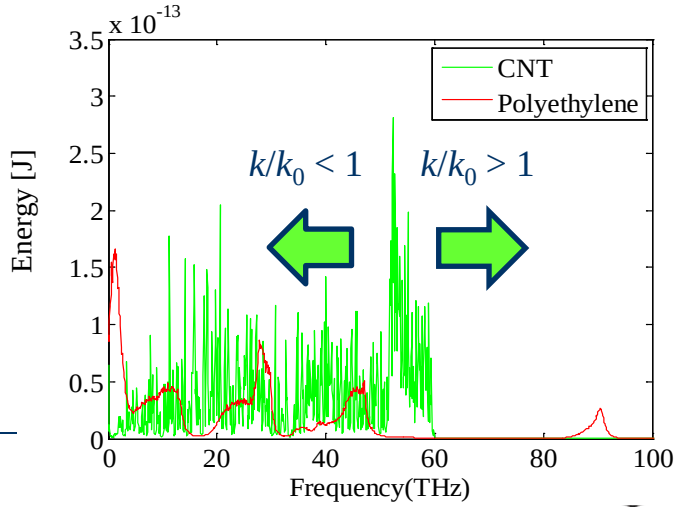


K decreases as force constants increase

Øncreasing mismatch between vibrational modes of CNT and PE

k/k_0	CNT power spectrum
Increase	Upshift
decrease	Downshift

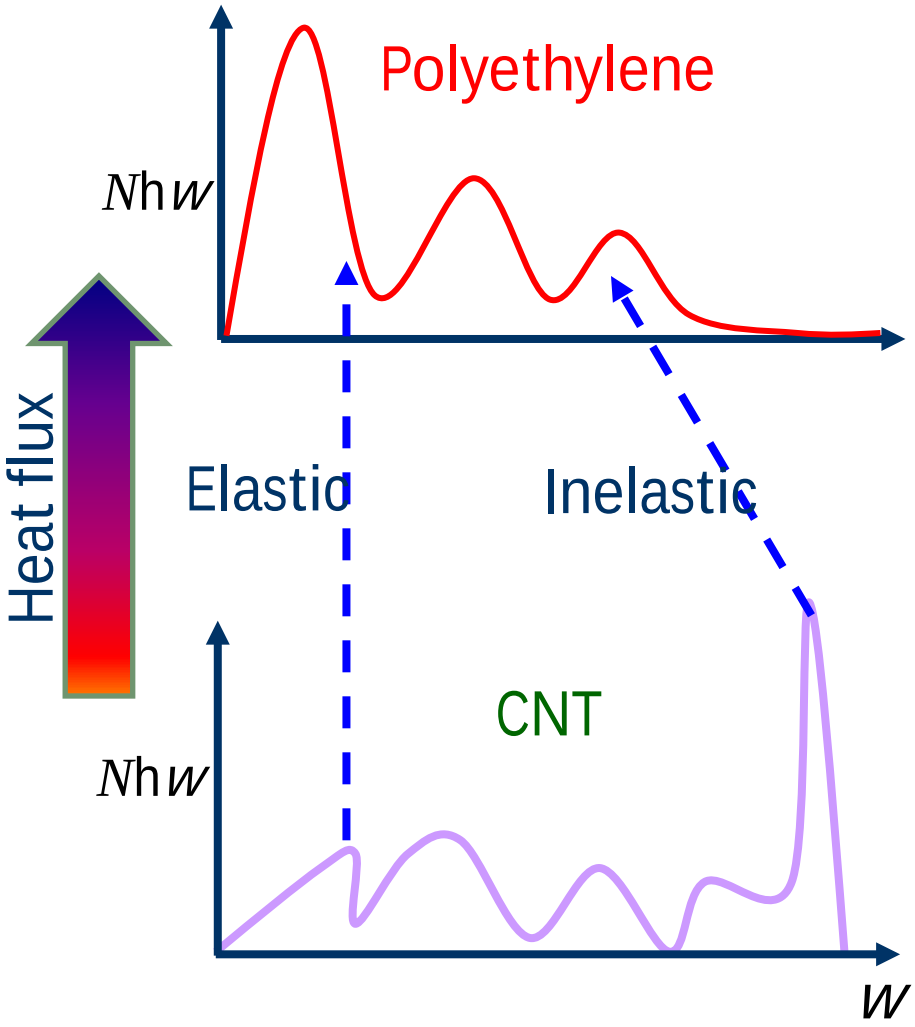
- Power spectra of CNT and polyethylene (k/k_0=1)



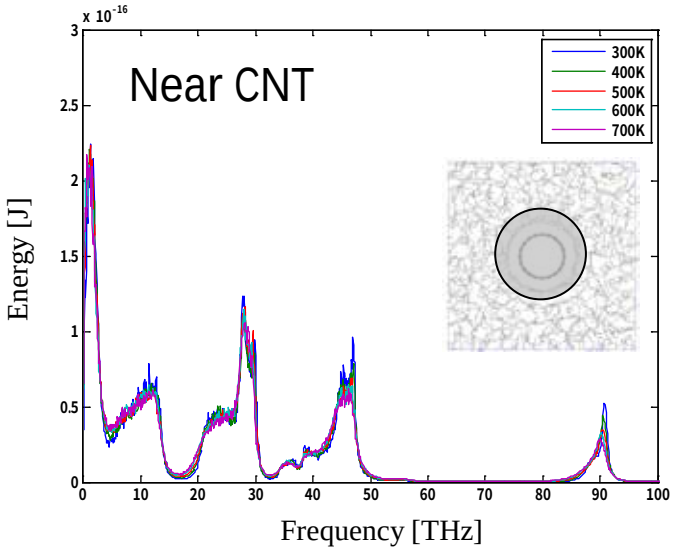
k_0 is original value in Universal Force Field

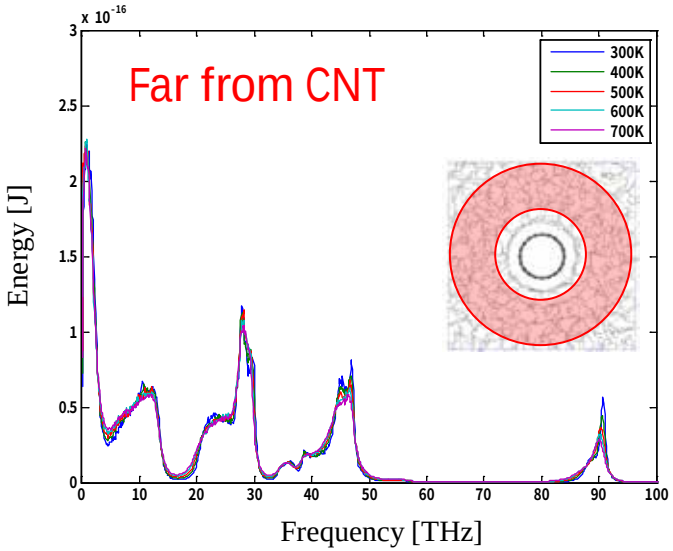
Elastic vs. inelastic conduction of lattice vibrations

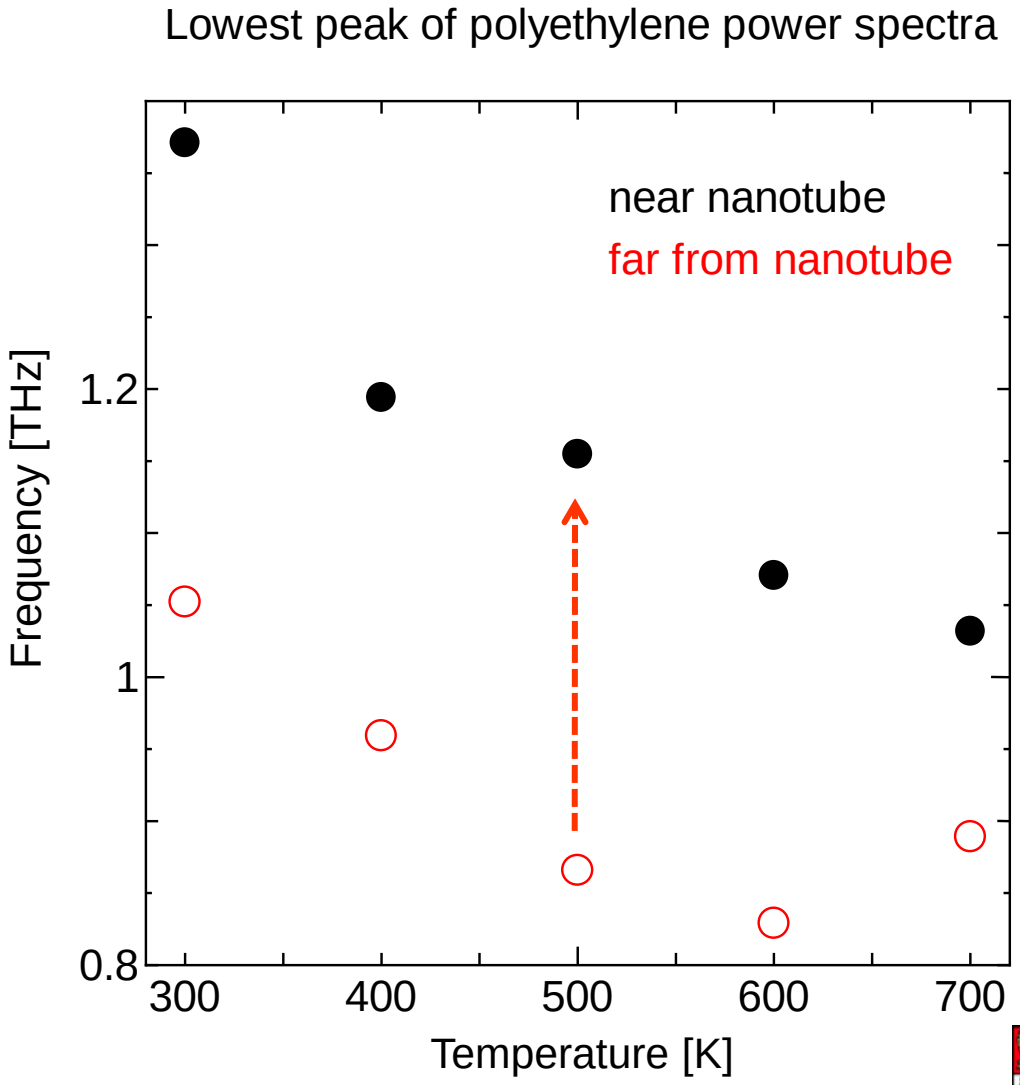
Thermal conductivity is JUNCTION DOMINATED



Frequency shift in PE power spectrum near CNT







Summary of mechanical and thermal property results

- Combined use of lattice model and reverse-mapped atomistic simulations give a fully relaxed composite morphology
- Even for PE-CNT composites with low interfacial energies, see a *clear ordered layering of polymer chains around CNTs*
- For *strong CNT-polymer interactions*, the ordered layer gives rise to *strong positive deviations from rule of mixtures* for low strain elastic properties
- CNT-polymer interactions also give rise to *localized upshift in frequency distribution close to tube surface*, enhancing the transfer of thermal energy from matrix to CNT
- Tune the boundary conductance to improve properties