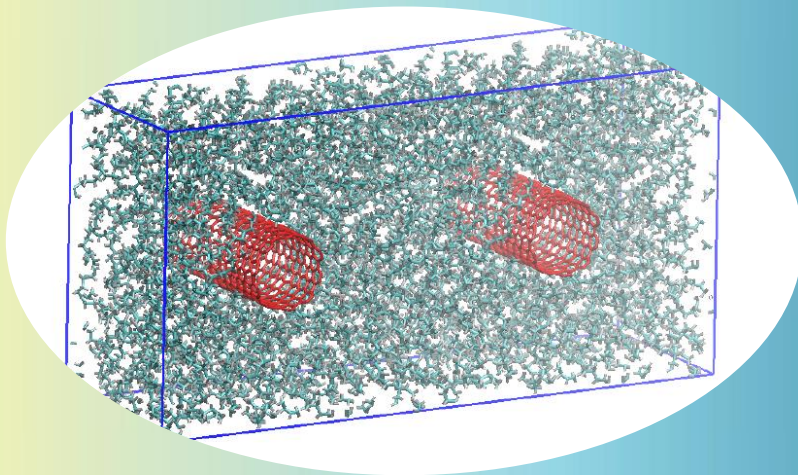


# Interfacial barriers to thermal transport in carbon nanomaterials and polymer- nanotube composites: a molecular modelling study



**James A. Elliott**

Macromolecular Materials Laboratory

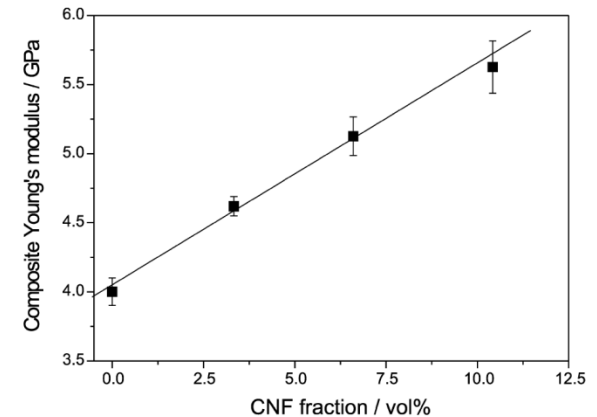
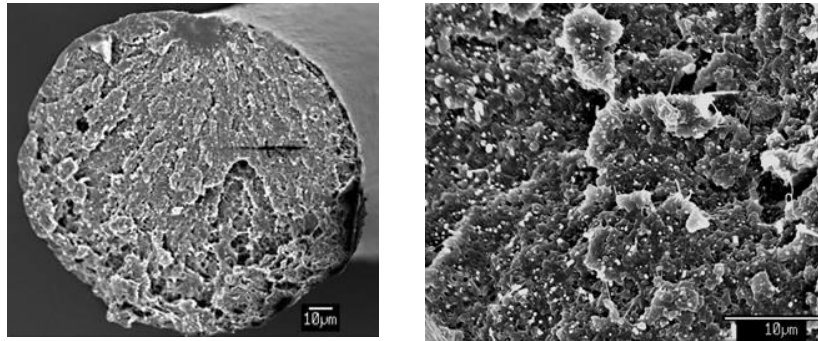
Department of Materials Science & Metallurgy

University of Cambridge

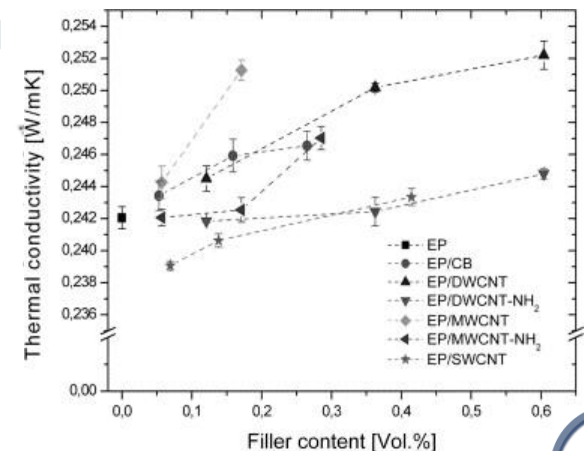
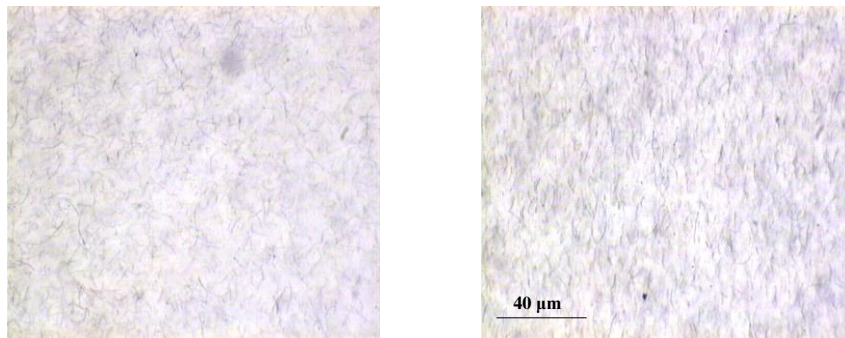
# Functional polymer nanocomposites

- Mechanical reinforcement and enhancement of electrical/thermal conductivity via incorporation of carbon nanotubes (CNTs)

Carbon nanofibre-reinforced PEEK fibres [1]



Alignment of MWCNTs in sheared epoxy resin [2]



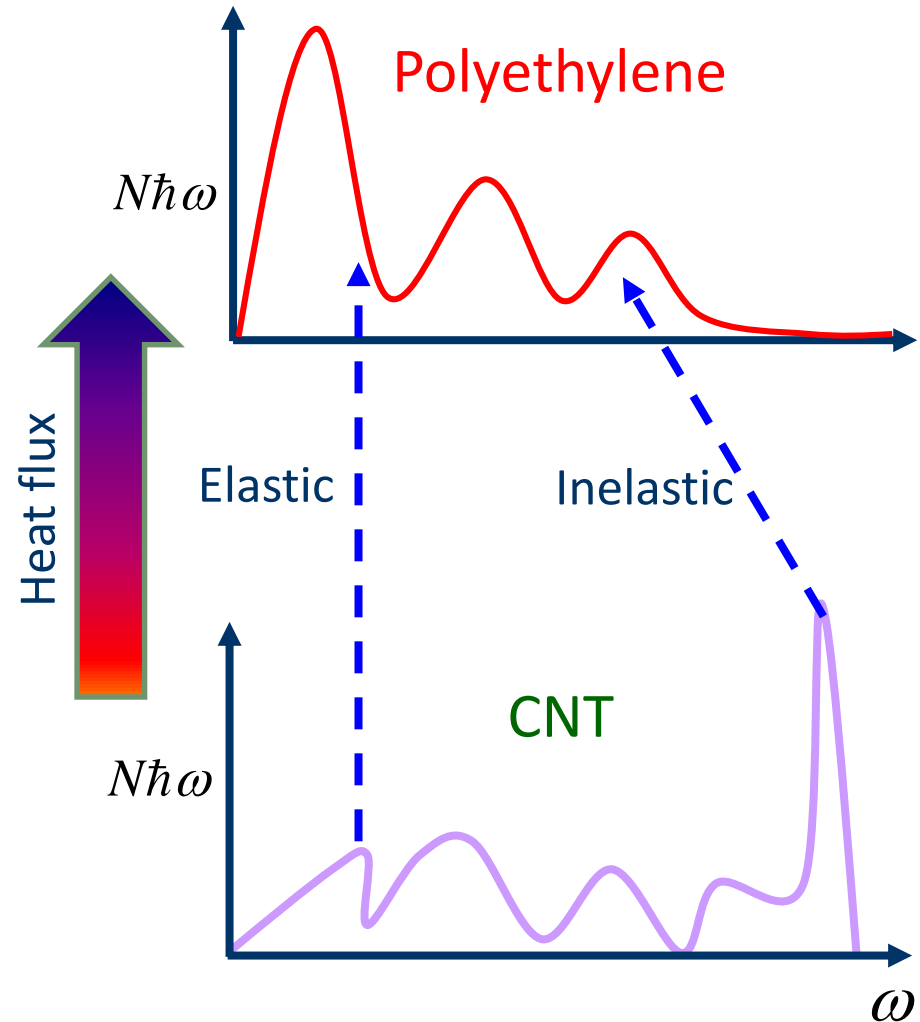
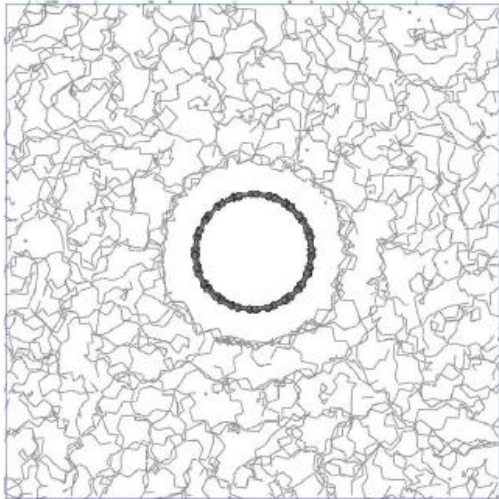
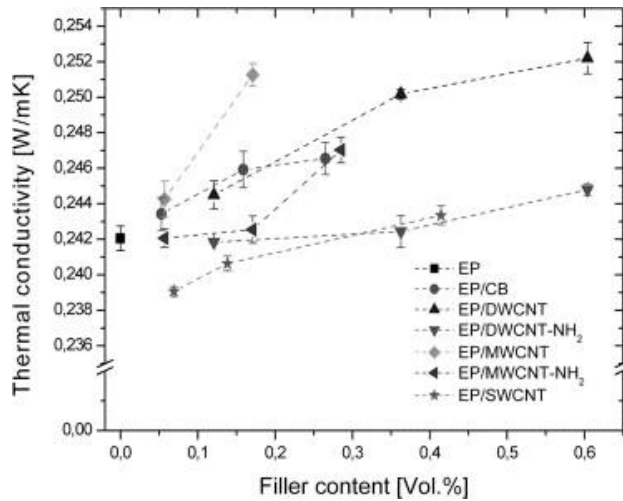
[1] J. Sandler, P. Werner, M.S.P. Shaffer et al. *Composites Part A* **33** 1033-1039 (2002)

[2] S.S. Rahatekar, K. Koziol, S.A. Butler, J.A. Elliott et al. *J. Rheology*, **50**, 599-610 (2006)



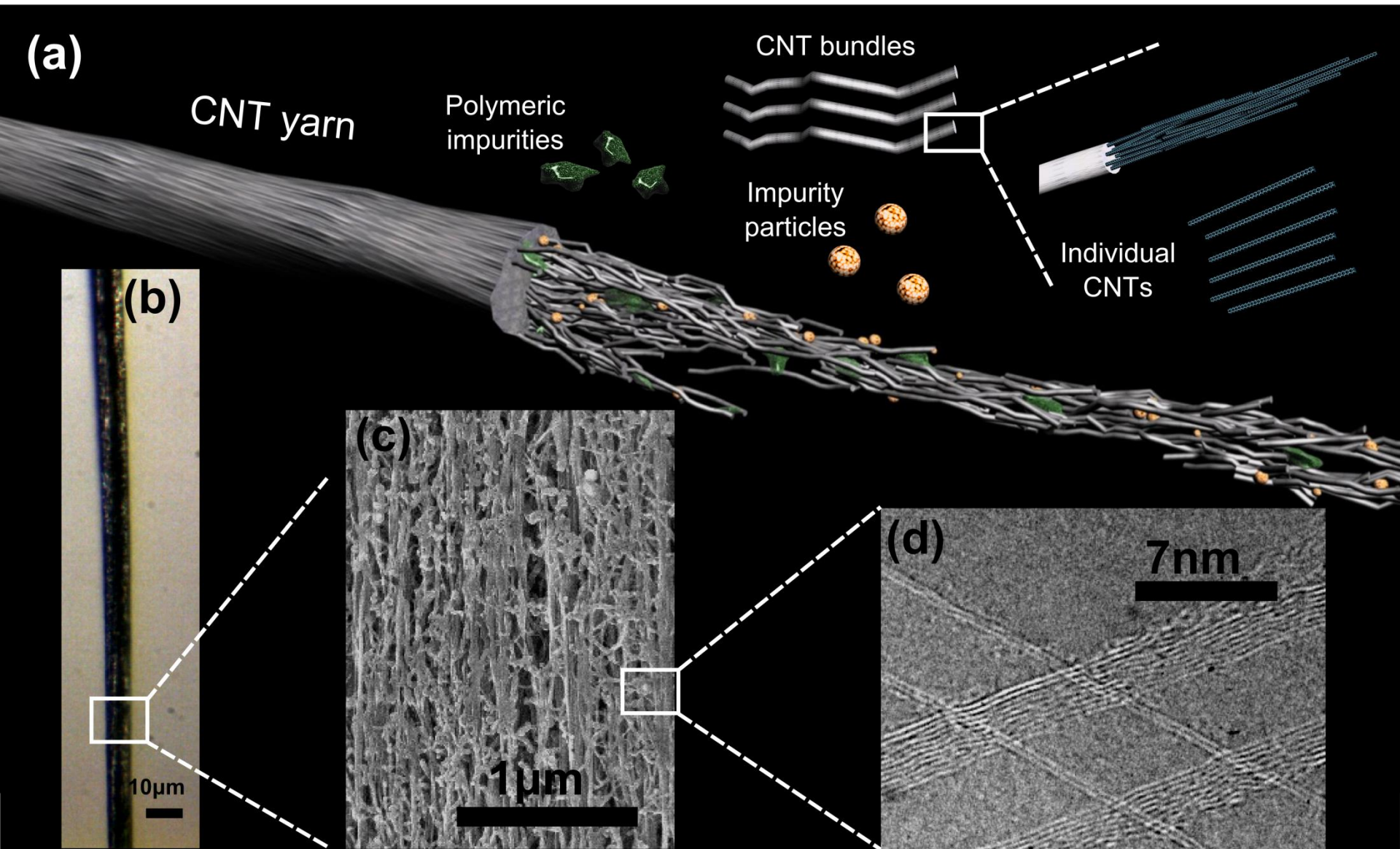
# Thermal vs. electrical conduction in CNT networks

Thermal conductivity is **INTERFACE DOMINATED** (Kapitza resistance)





# CNT Yarns made by Cambridge CCVD process

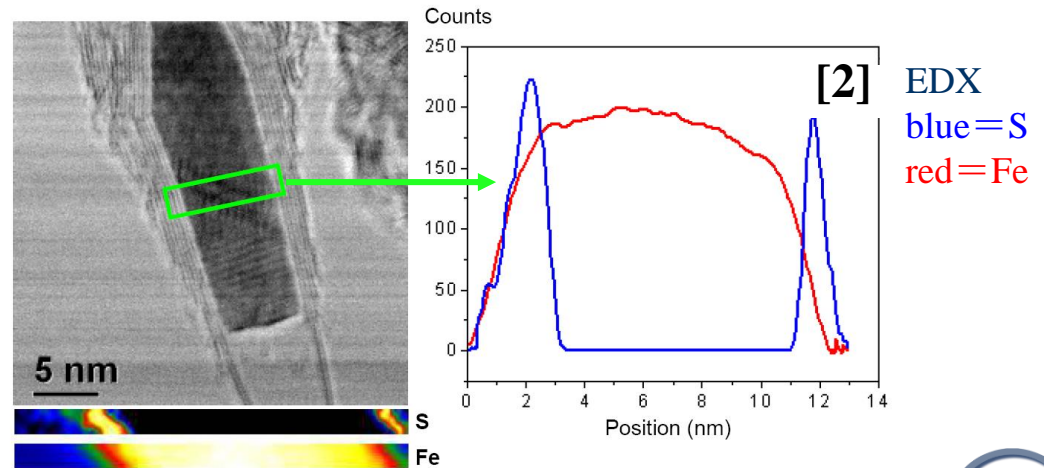
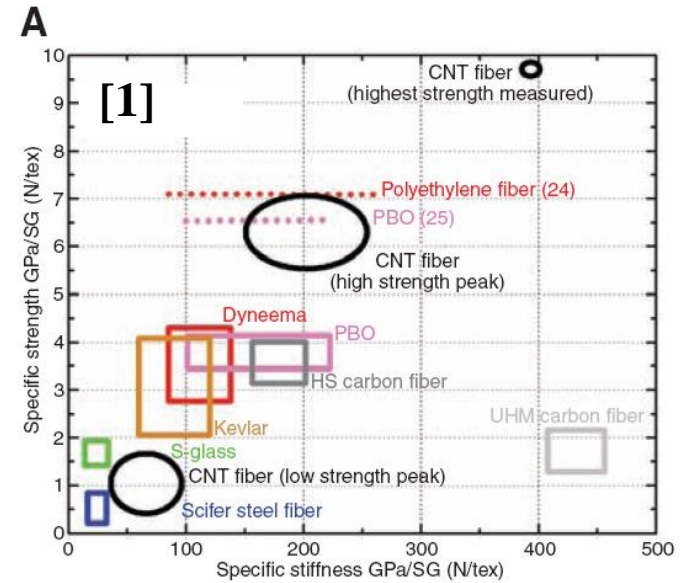
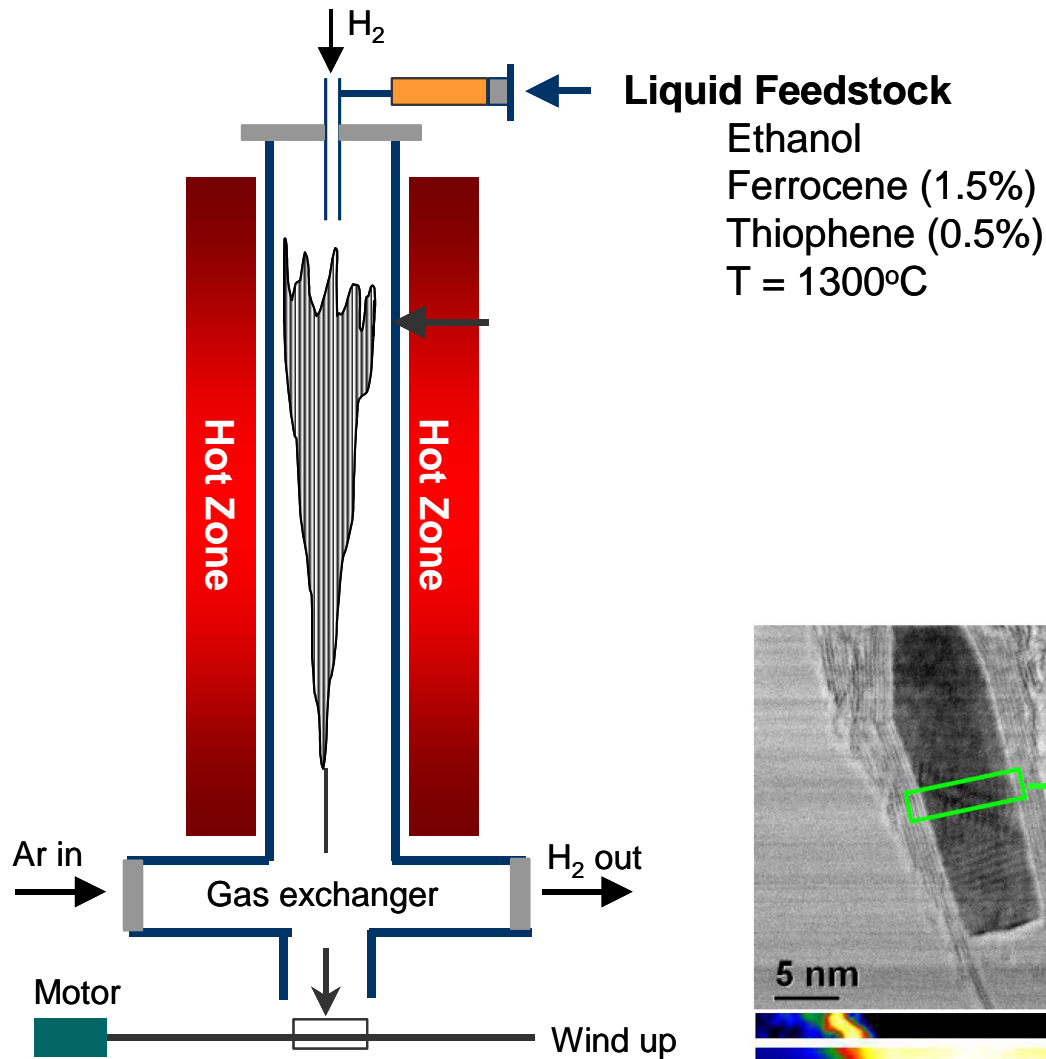


[1] Motta, et al. *Advanced Materials*, **19**, 3721-3726 (2007).

[2] Koziol et al., *Science*, **318**, 1892-1895 (2007).



# High-temperature CNT 'fibre' process

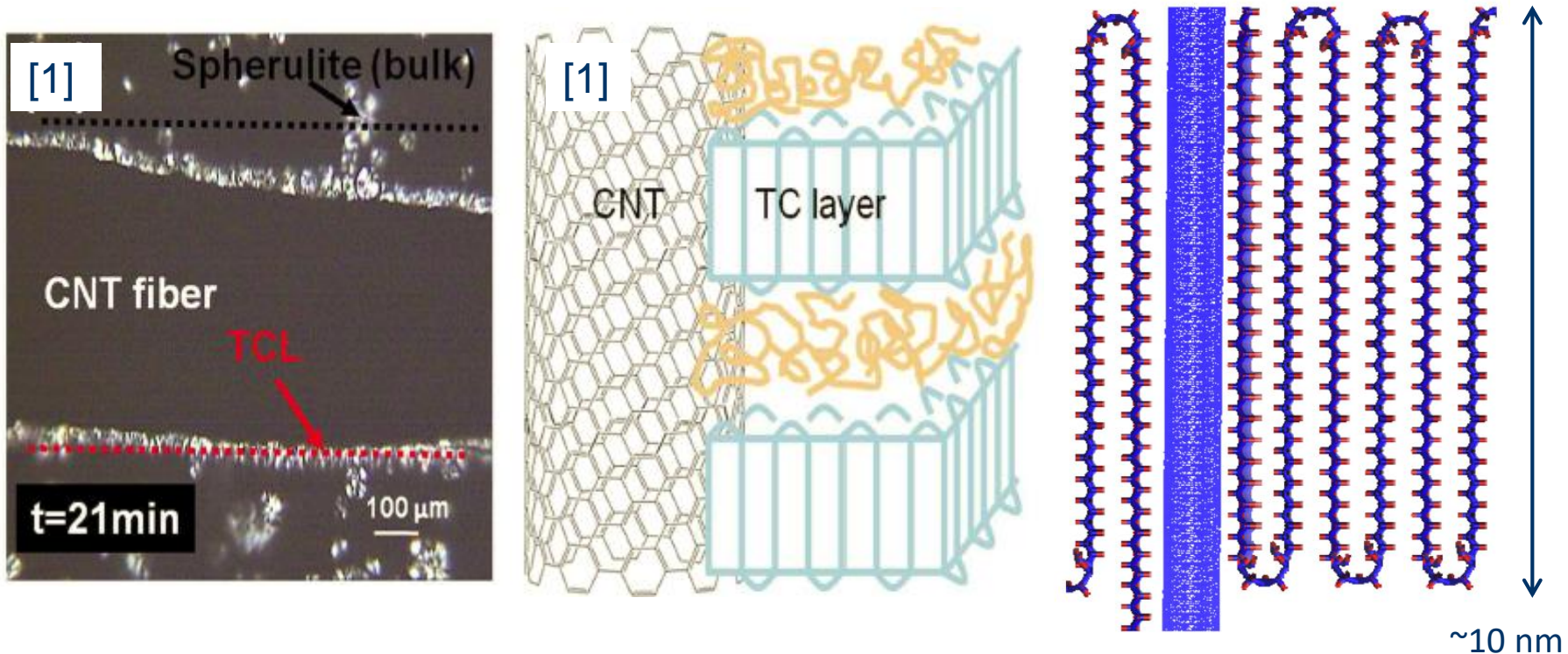


[1] K. Koziol et al. *Science* **318**, 1892-1895 (2007).

[2] M.S. Motta, A. Moisala, I.A. Kinloch and A.H. Windle *J. Nanosci. Nanotech.* **8**, 2442-2449 (2008).



# Transcrystallinity in CNT(fiber)-polymer composites



- Transcrystalline layer (TCL) of polymer forms near interface with CNT fiber due to fast heat transfer because of faster cooling rate than in bulk
- Effect on thermal boundary resistance?



# Lattice MC model of amorphous polymer matrix

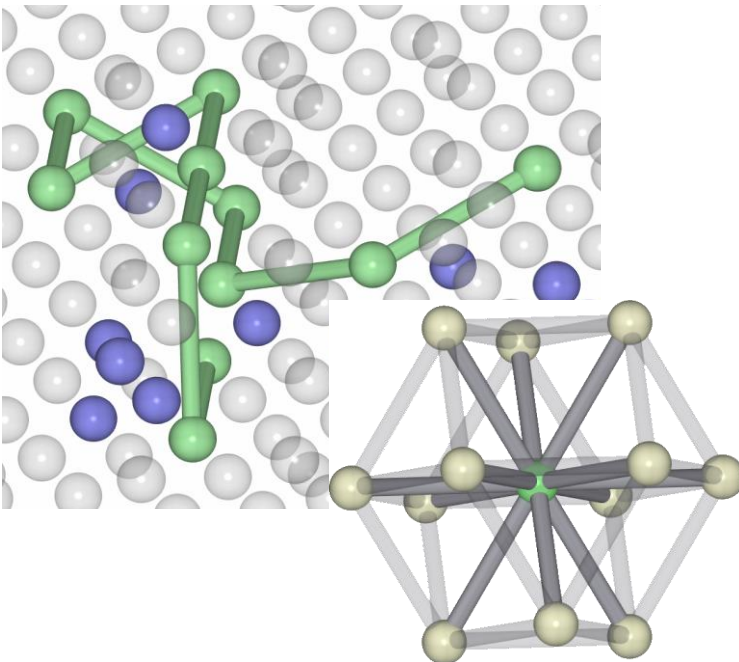
Polymer represented by connected sites (beads) on face-centred cubic lattice

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

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

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

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

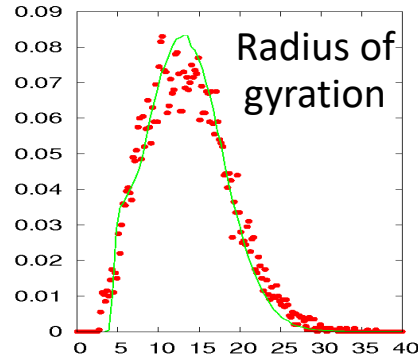
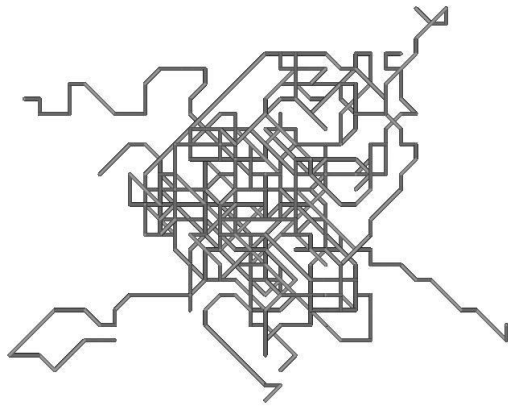


[1] K.R. Haire *et al.*, *Comput. Theor. Polym. Sci.*, **11**, 17 (2001)

[2] F.Wang and D.P. Landau, *Phys. Rev. Lett.*, **86**, 2050 (2001)



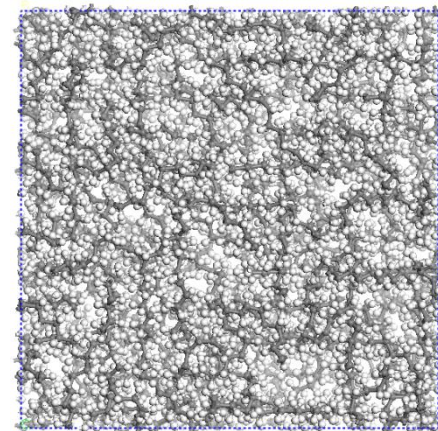
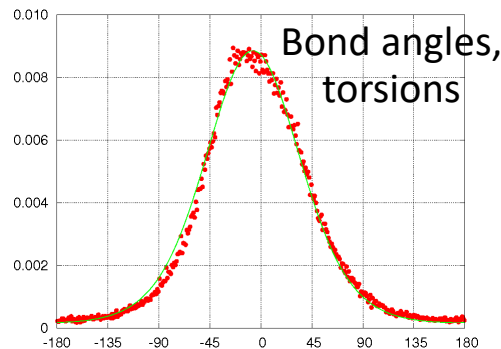
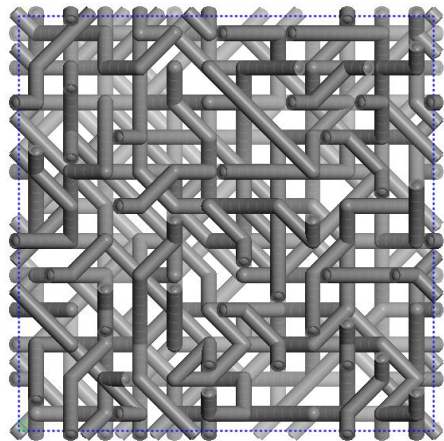
# Lattice MC model of amorphous polymer matrix



mapping



reverse-mapping  
(RM)



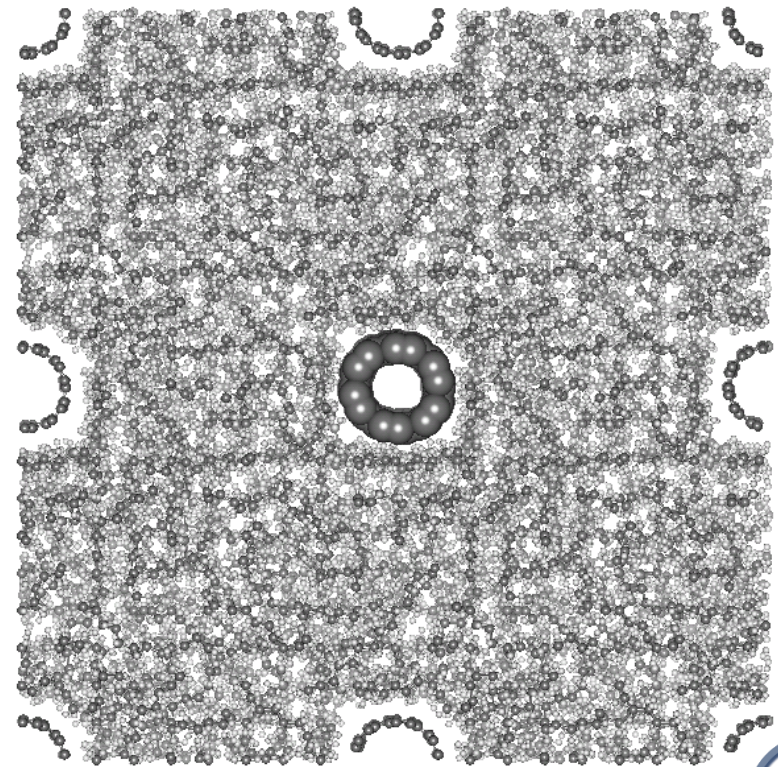
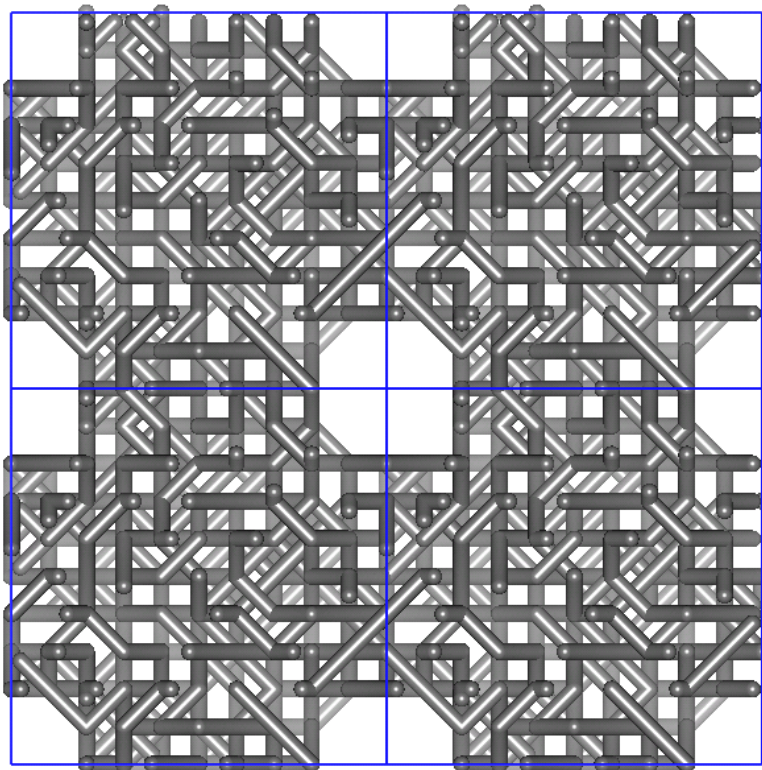
[1] J. Baschnagel et al. *Adv. Polym. Sci.* **152**, 41-156 (2000)

[2] F. Müller-Plathe *ChemPhysChem* **3**, 754-769 (2002)



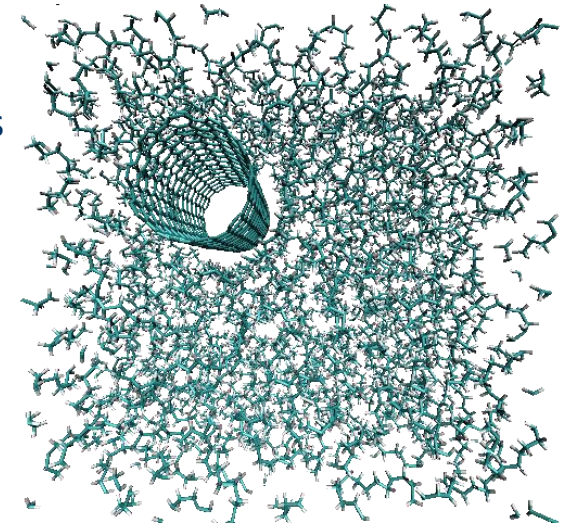
# Lattice MC model of amorphous PE/CNT composite

- 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.

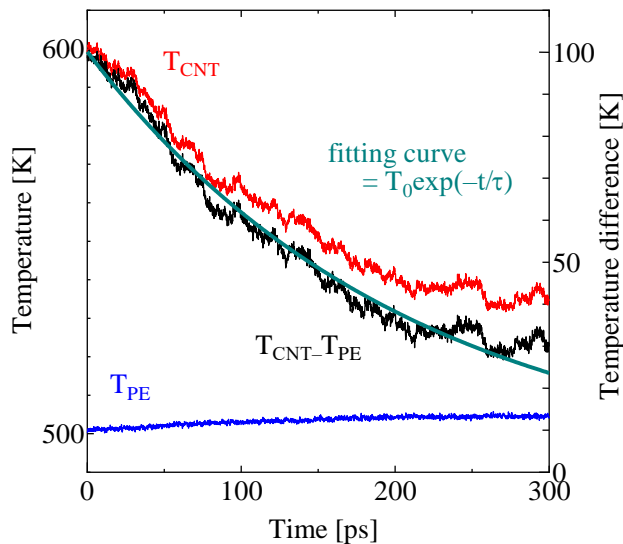


# Interfacial heat transfer between CNT and PE

- System
  - A (10,10) single wall carbon nanotube (CNT) and amorphous polyethylene chains (figure on the right)
- Force field
  - CNT : Tersoff potential optimized for phonon spectra <sup>1</sup>
  - Polyethylene : Polymer Consistent Force Field <sup>2</sup>



## Lumped heat capacity method <sup>3</sup>



- 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)

$$K = \frac{1}{\left( \frac{1}{m_{\text{CNT}} c_{\text{CNT}}} + \frac{1}{m_{\text{PE}} c_{\text{PE}}} \right) S \times \tau}$$

$m$  : total mass in the system

$c$  : heat capacity

$S$  : interface surface area

$\tau$  : relaxation time

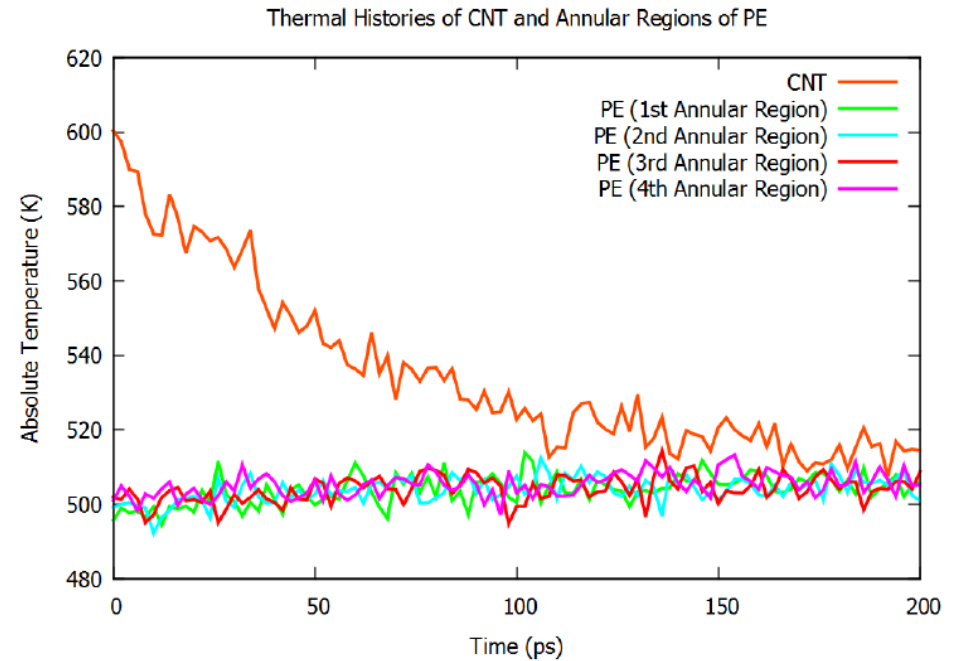
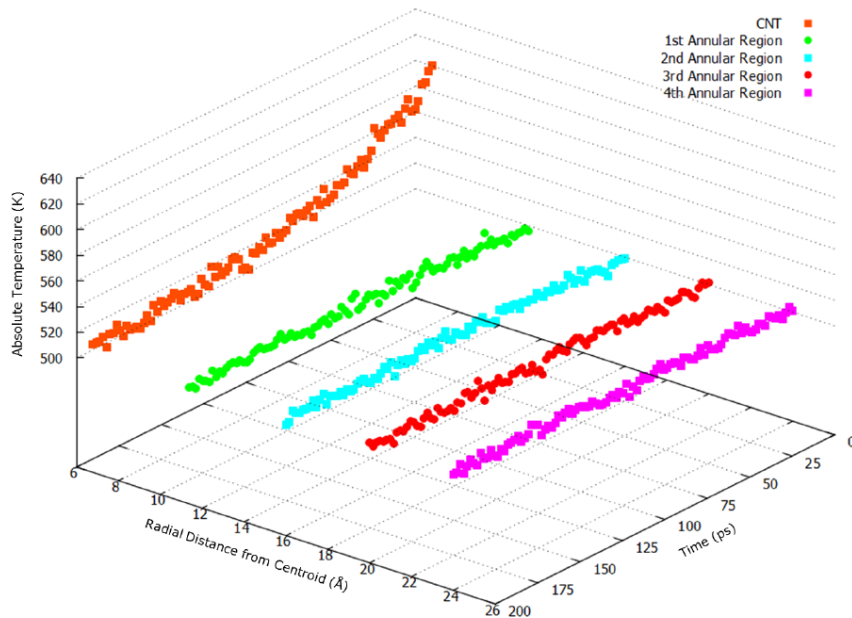
[1] S. Hida, T. Hori, T. Shiga, J. A. Elliott, J. Shiomi, *Int. J. Heat Mass Transfer*, **67**, 1024-1029 (2013)

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



# Validation of lumped heat capacity method

- Lumped heat capacity method depends on assumption that heat transfer is 1D – no thermal gradients parallel to CNT axis



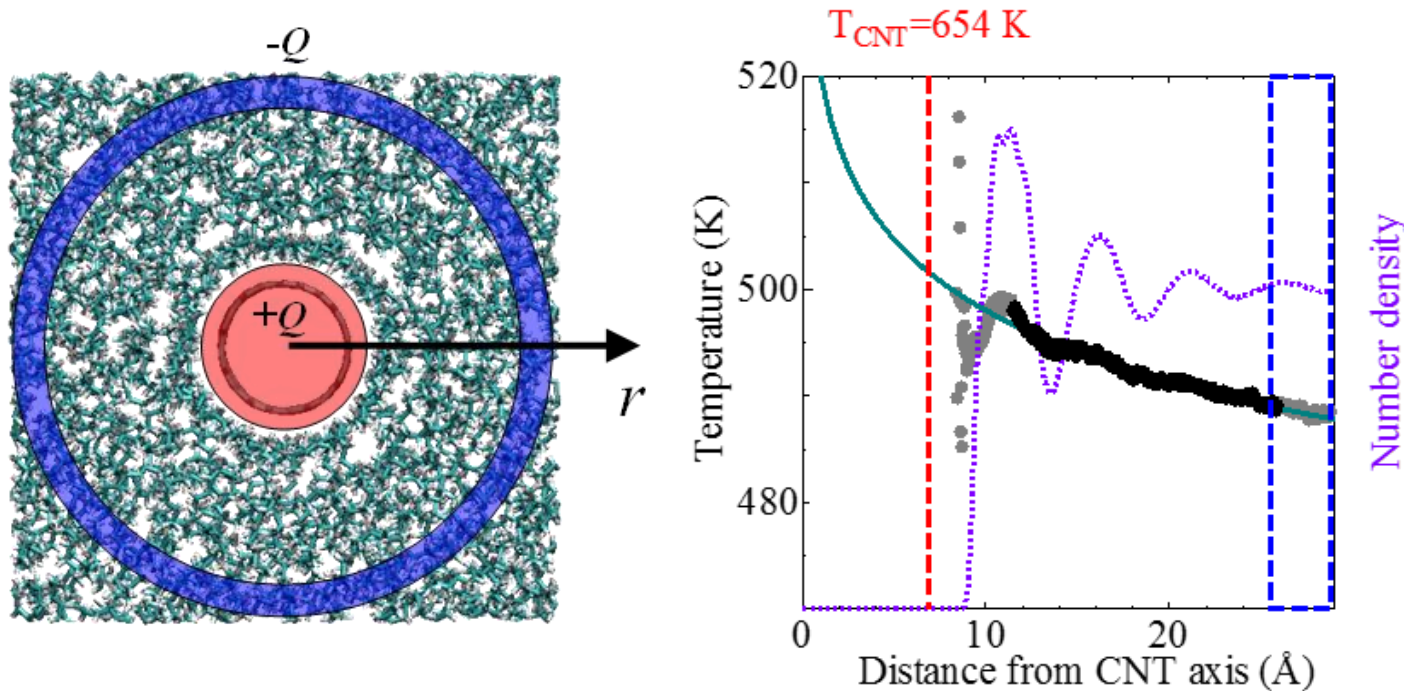
- Temperature of PE rises uniformly with time, and evenly in space (no gradients, except perpendicular to CNT axis)
- Reason is that thermal conductance of CNT  $\gg$  that of PE





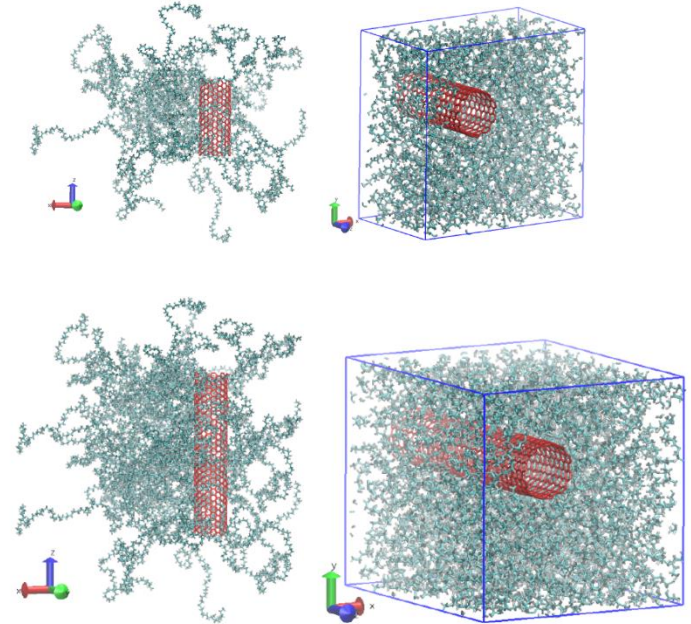
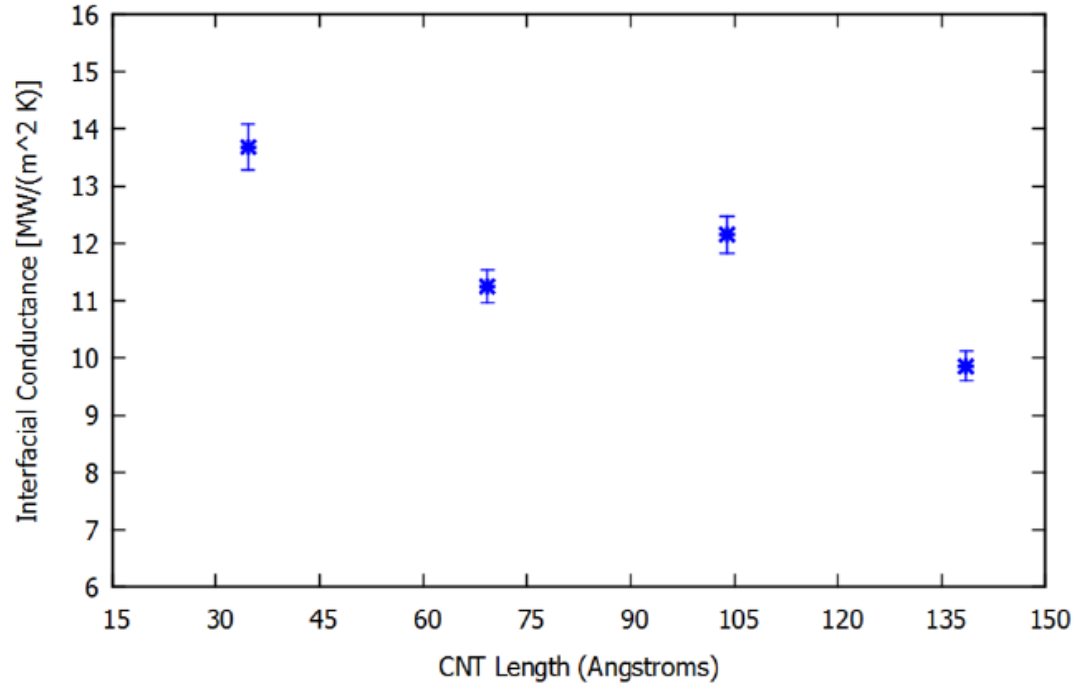
# Validation of lumped heat capacity method

- TBC calculated independently from steady-state method yields value consistent with non-equilibrium method



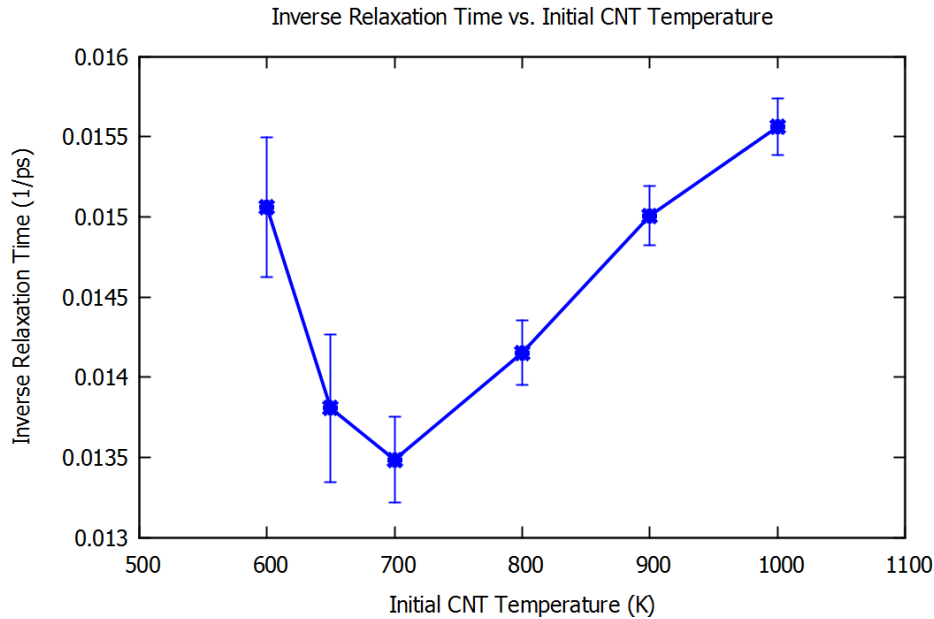
# CNT-PE TBC as function of CNT length

Interfacial Conductance vs. CNT Length

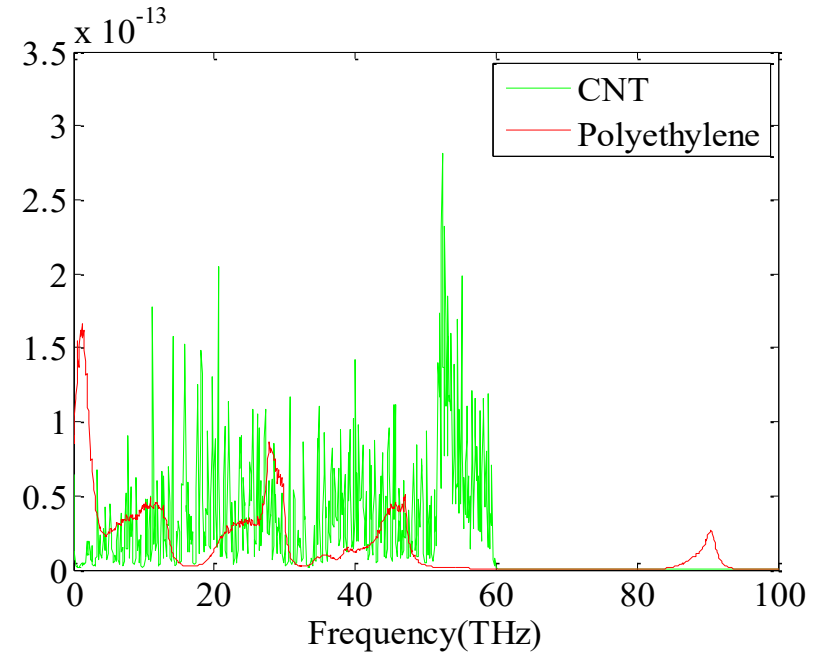


- All simulations have similar structure in outer layers of PE, irrespective of CNT length
- TBC appears to be converging (in oscillatory manner) on limiting value for “long tube”

# Effect of CNT temperature on TBC



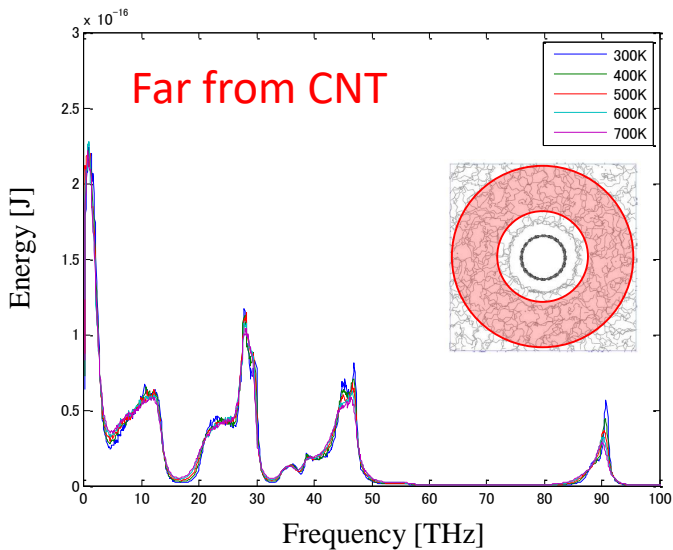
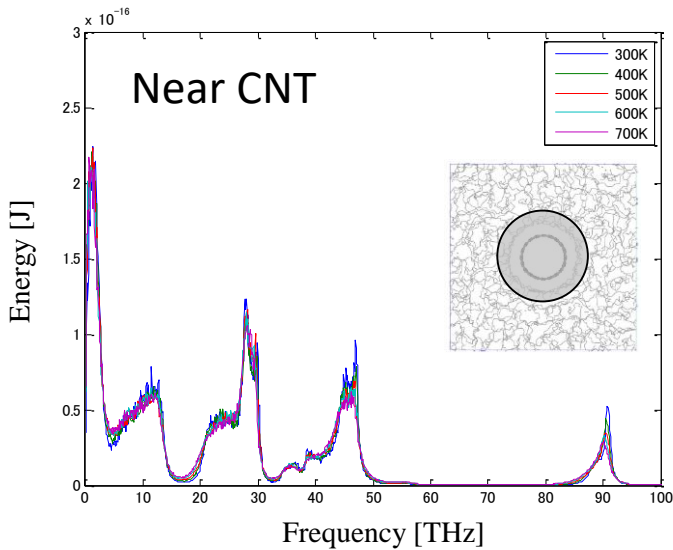
Phonon power spectra of CNT and polyethylene



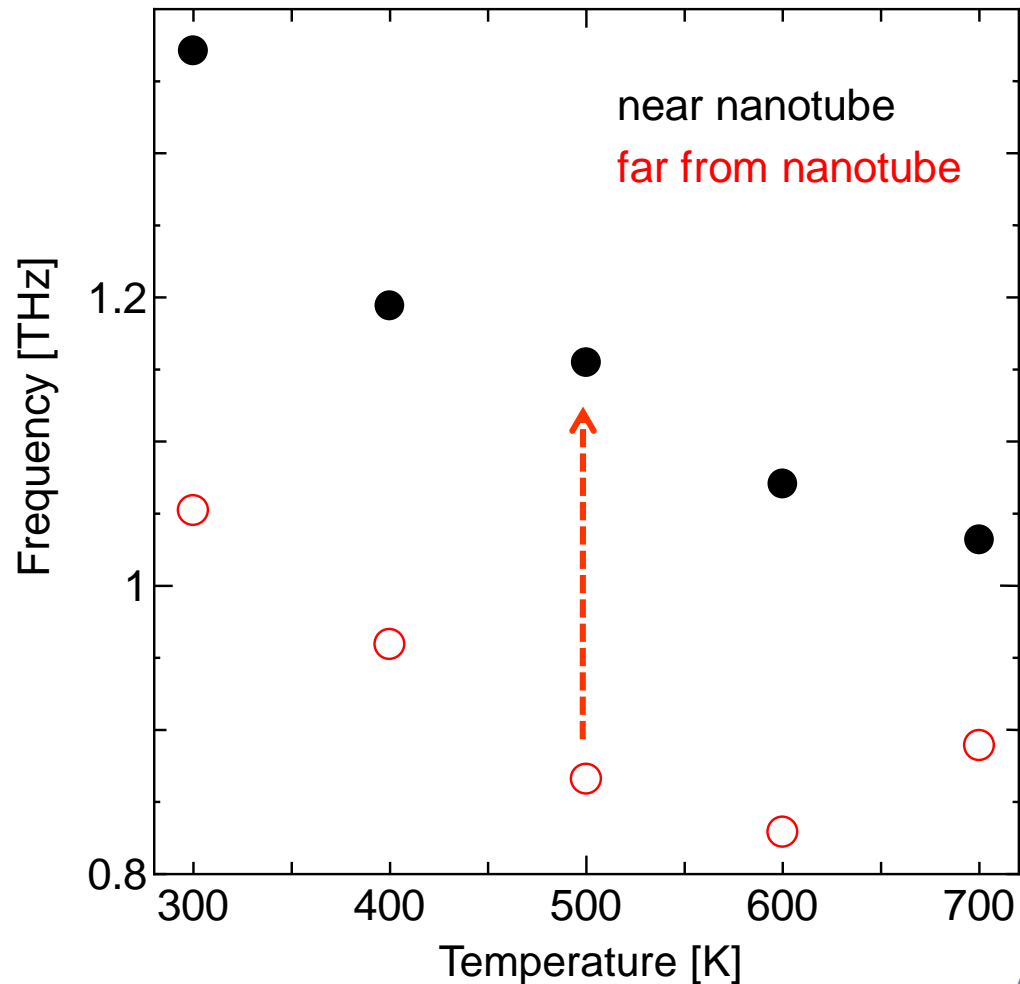
- Non-monotonic behaviour of TBC with temperature due to non-linear phonon scattering processes occurring at higher temperatures (> 720 K)



# Frequency shift in PE power spectrum near CNT



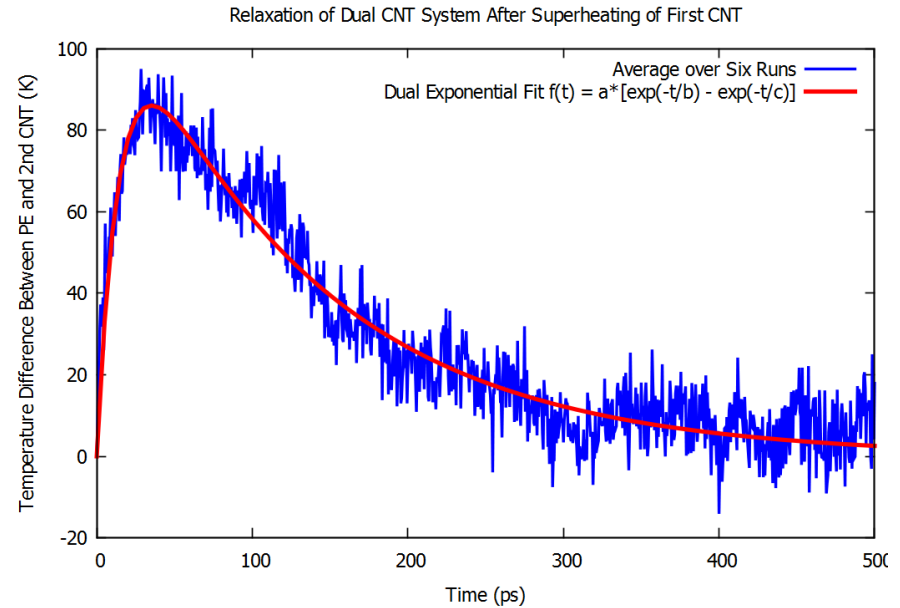
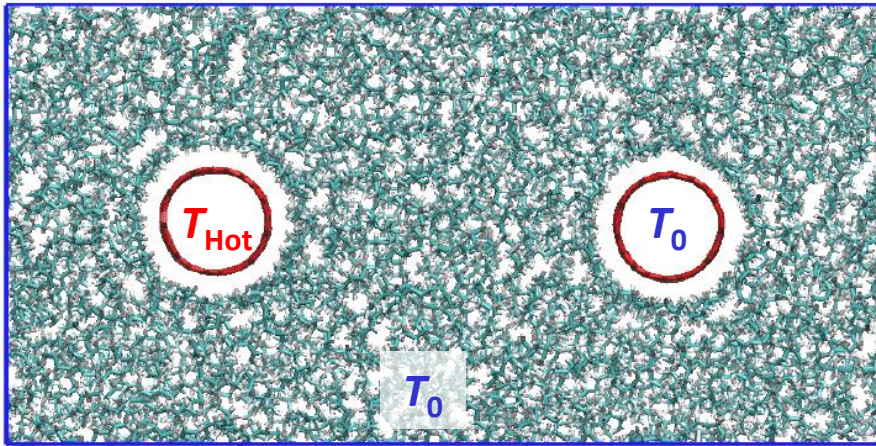
Lowest peak of polyethylene power spectra



[1] S. Hida, T. Hori, T. Shiga, J. A. Elliott, J. Shiomi, *Int. J. Heat Mass Transfer*, **67**, 1024-1029 (2013).



# Dual CNT system – heat transfer from hot to cold tube



$$\Delta T(t) = \left( \frac{T_{\text{Hot}} - T_0}{2} \right) \left( e^{\lambda_2 t} - e^{\lambda_1 t} \right).$$

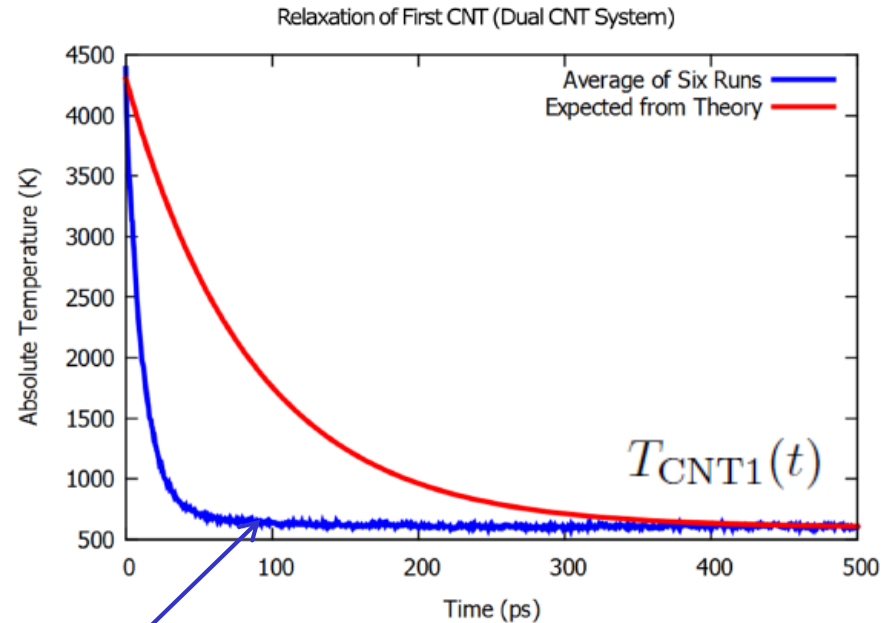
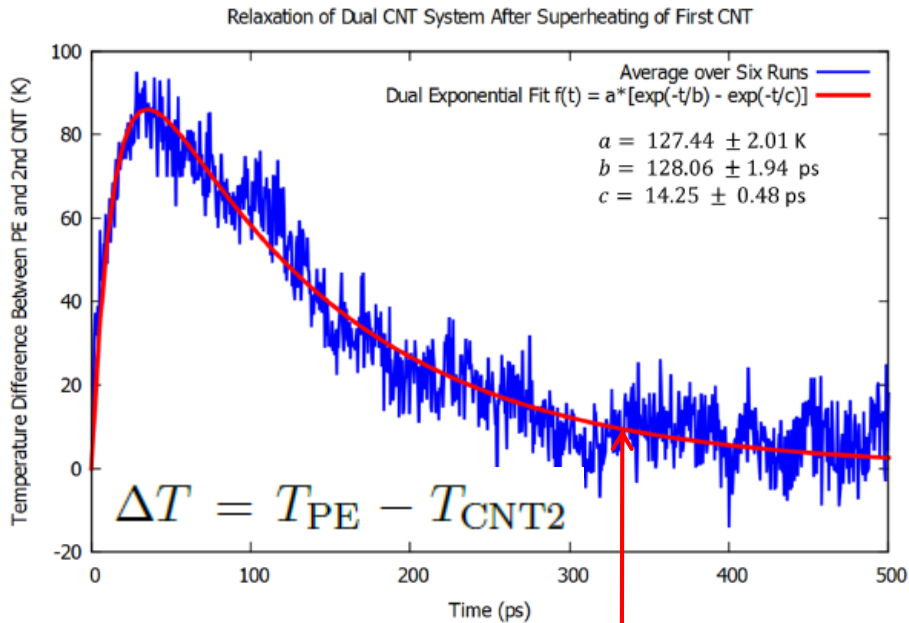
$$\tau_1 = |\lambda_1|^{-1} \text{ and } \tau_2 = |\lambda_2|^{-1}$$

$$T_0^{\text{PE}} = 500 \text{ K}, T_0^{\text{CNT}2} = 500 \text{ K}, \text{ and } T_0^{\text{CNT}1} = T_{\text{Hot}}$$

$$T_{\text{Hot}} \approx 4400 \text{ K}$$



# Dual CNT system – heat transfer from hot to cold tube



$$K_1 \approx 10.6 \pm 0.2 \text{ MW}/(\text{m}^2 \text{ K})$$

from  $b = \tau_2 = \frac{C_{CNT}}{KA}$ ,

$$K_2 \approx 90.3 \pm 3.2 \text{ MW}/(\text{m}^2 \text{ K})$$

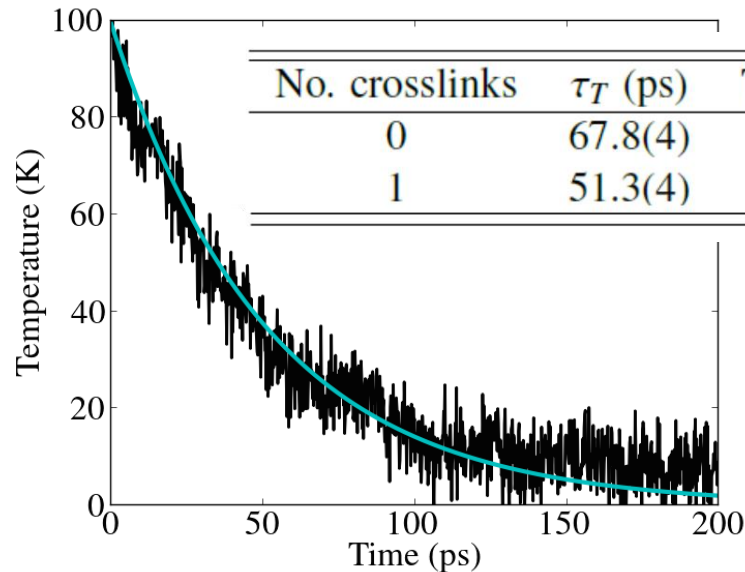
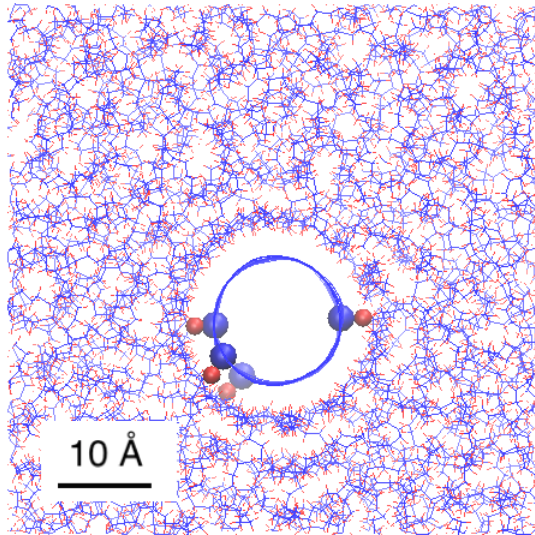
from  $c = \tau_1 = \frac{1}{\left(\frac{2}{C_{PE}} + \frac{1}{C_{CNT}}\right) KA}$ .





# Effect of crosslinking on TBC

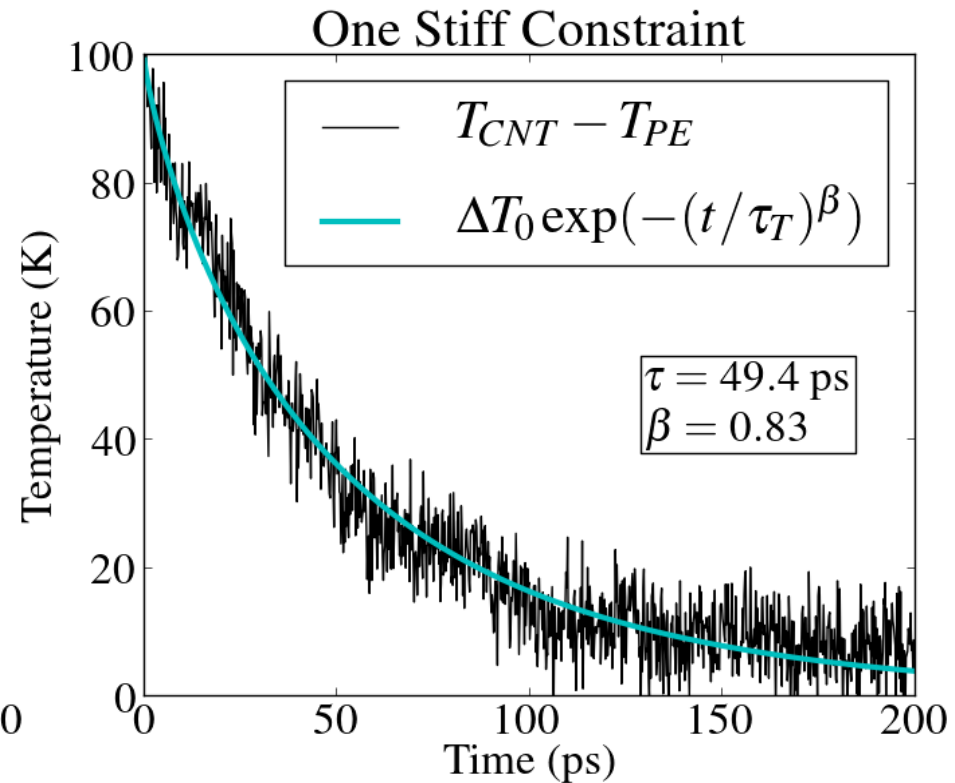
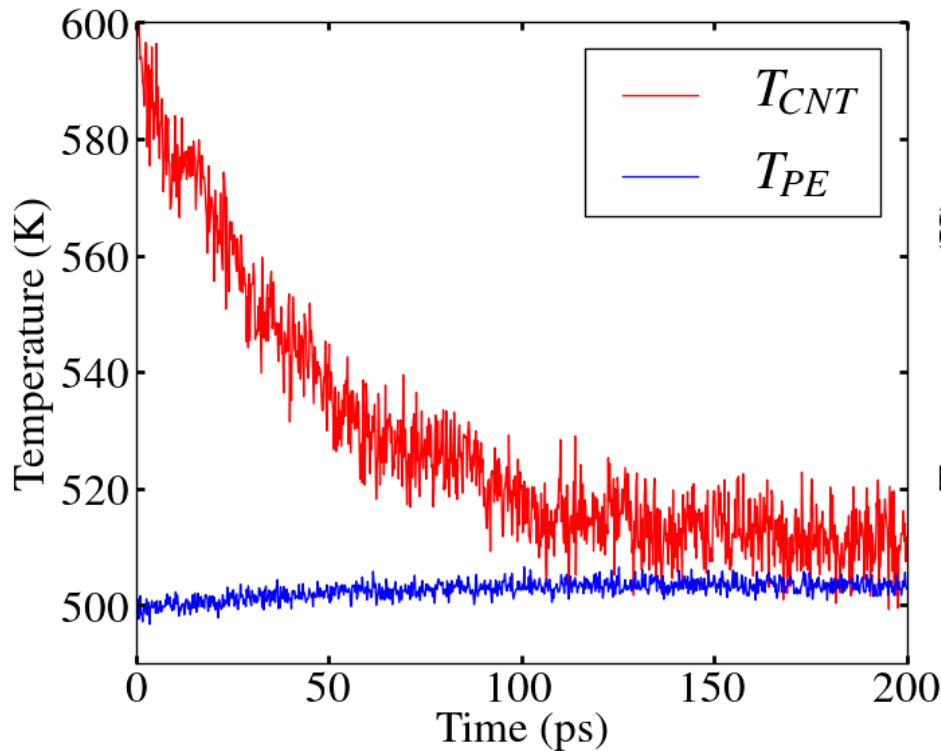
- Increase TBC by adding covalent links between CNT and polymer?



- Crosslinked structures do indeed show faster thermal relaxation
- Crosslinks can be either rigid constraints, or harmonic bonds with variable stiffness (spring constant)
- Also, vary the crosslink density (number of cross-links)

# Effect of crosslinking on TBC

- Some evidence that a *stretched exponential* fits better at longer time scales, possibly indicating multiple relaxation process

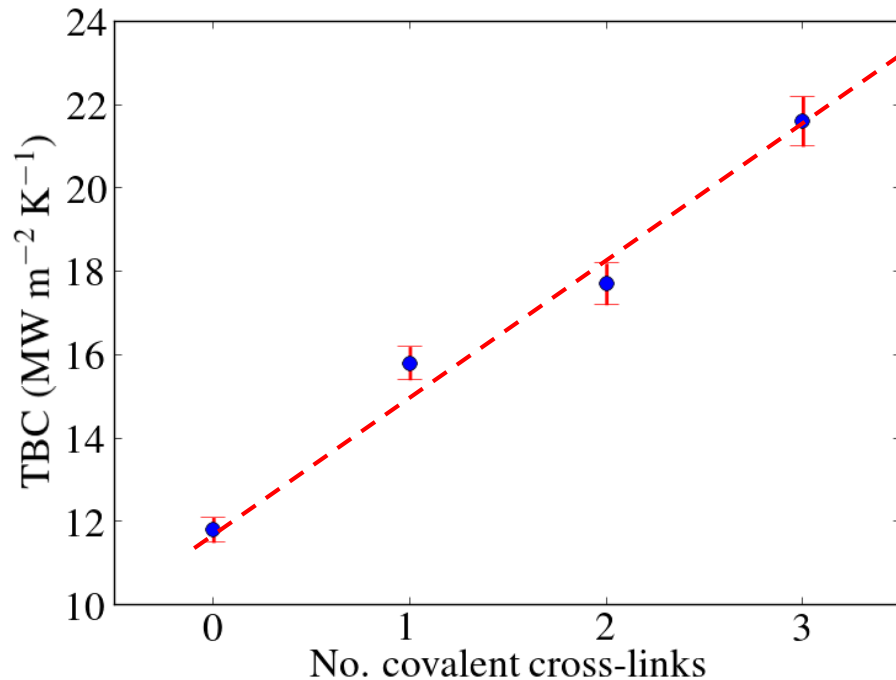


# Effect of cross-linking on TBC: stiff cross-links

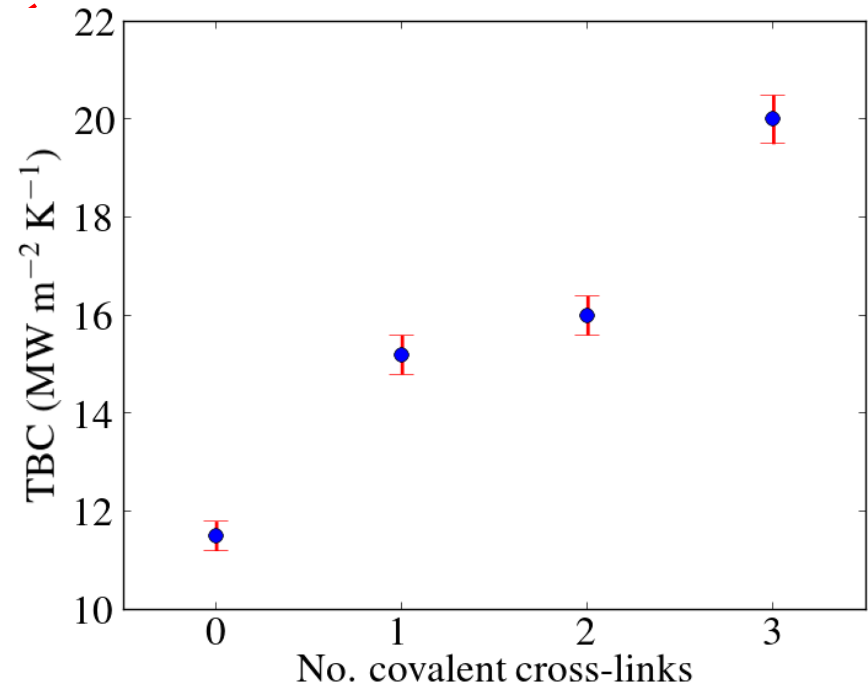
~ 40 links

- Vary number of stiff (rigid) cross-link bonds

Regular exponential fit



Stretched exponential fit

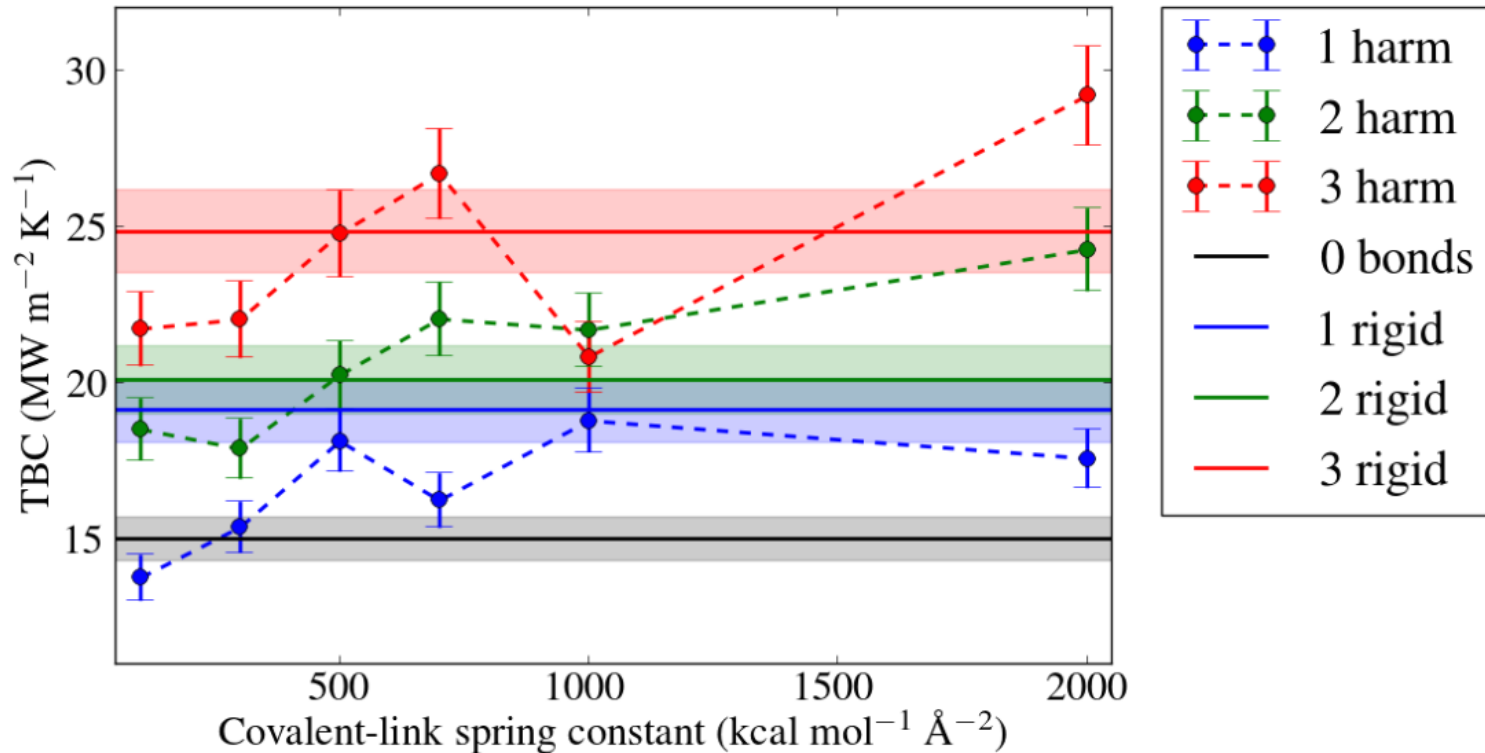


- TBC about 1 order of magnitude below the “perfect interface” limit, no sign of saturation at low cross-link densities



# Effect of crosslinking on TBC: harmonic crosslinks

- Vary stiffness (spring constant) of a *single* harmonic cross-link

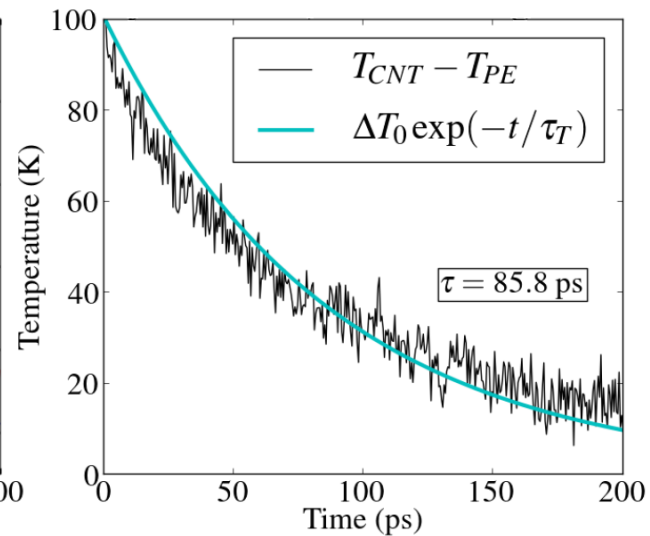
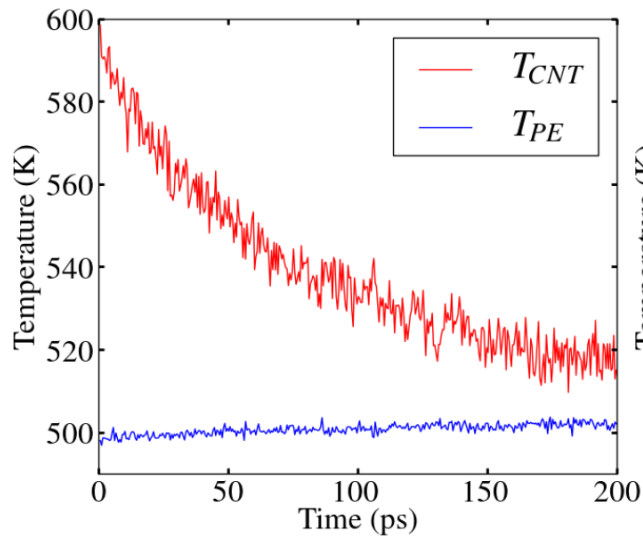
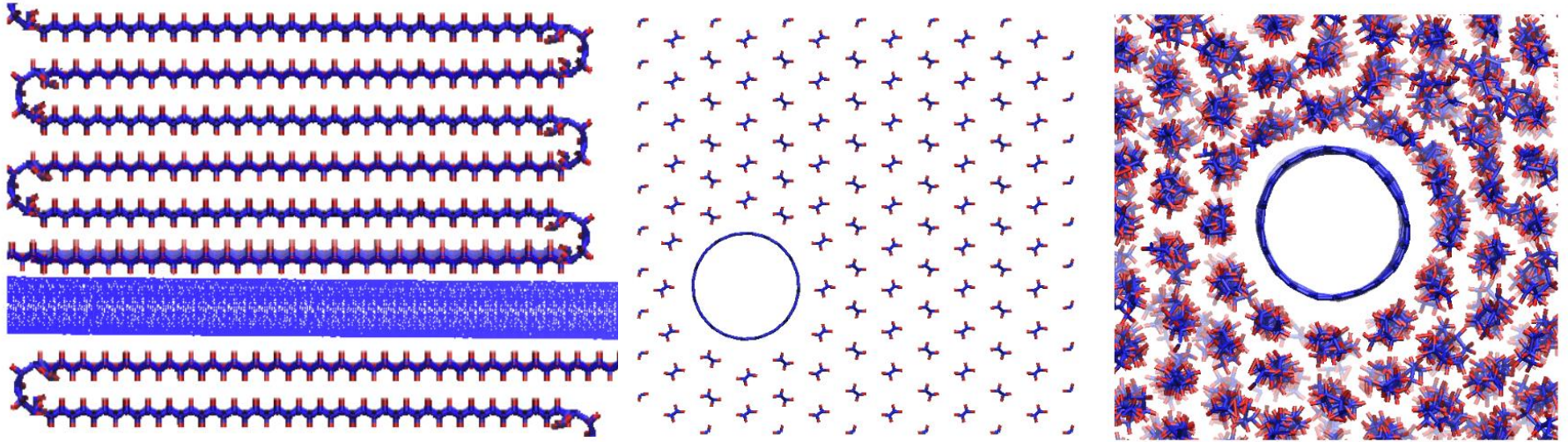


- Behaviour of TBC in rigid link limit surprising: in some cases, obtain a higher value of TBC for soft crosslink!

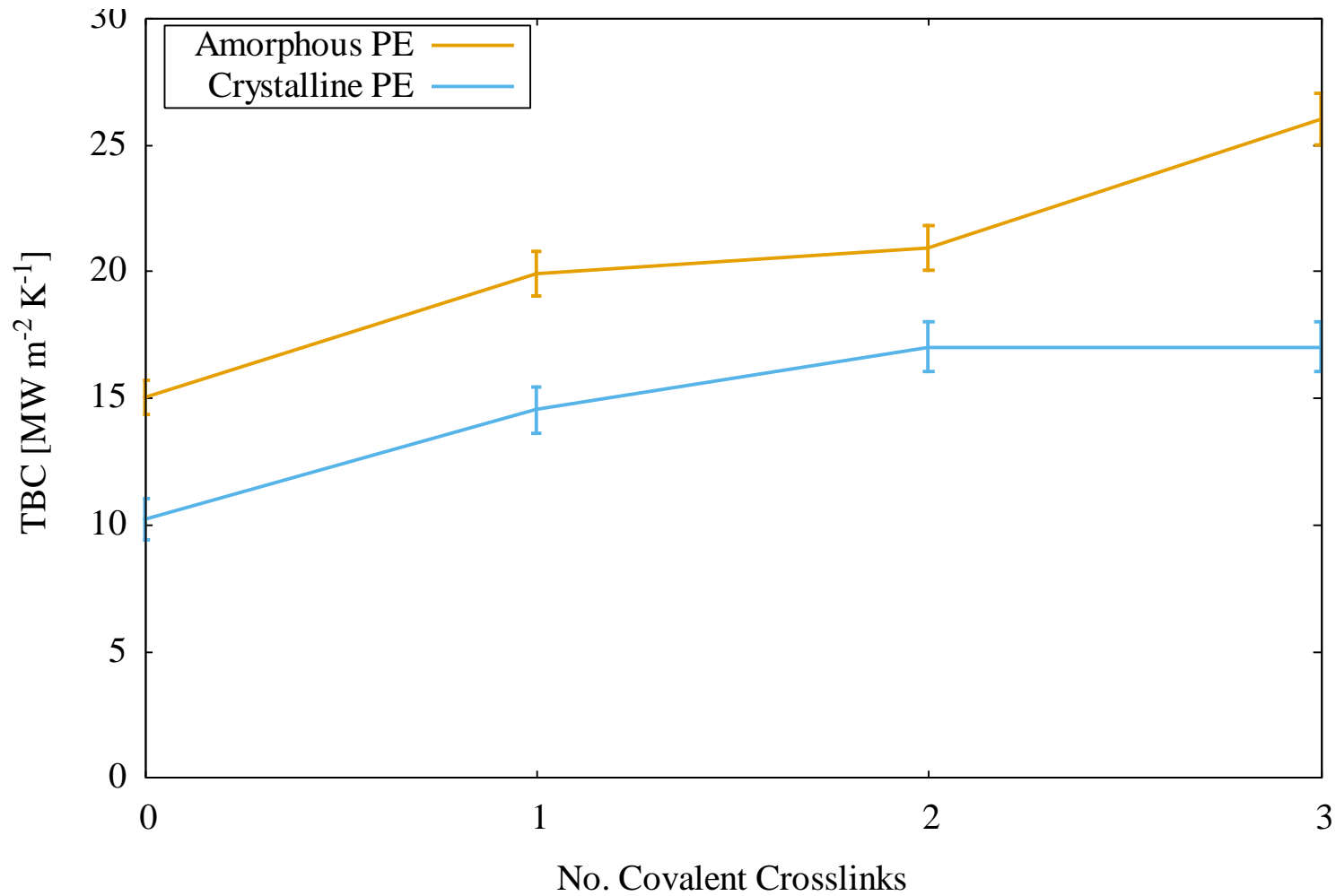




# Effect of transcrystalline PE layer around CNT

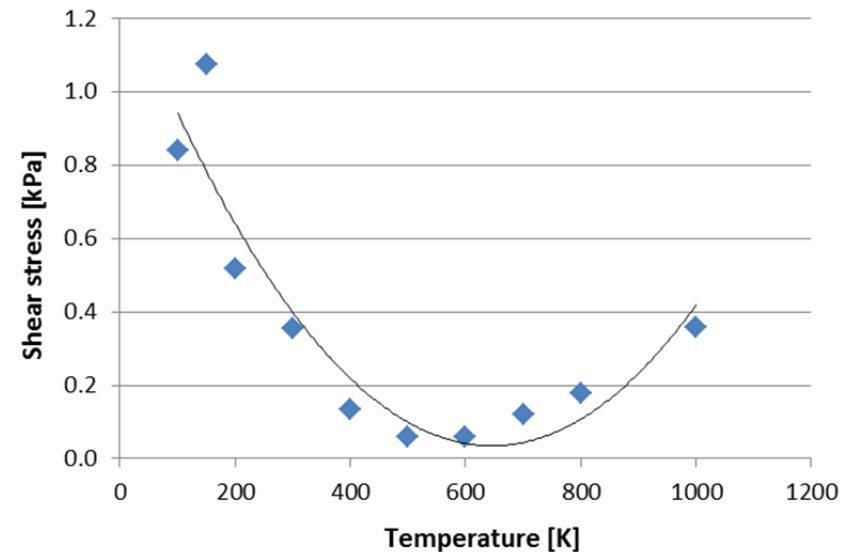
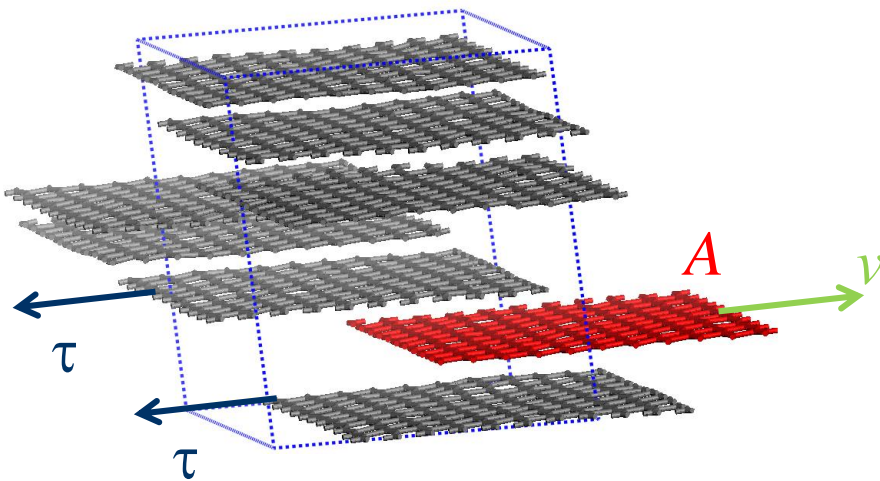


# Comparison of TBC for amorphous and crystalline PE



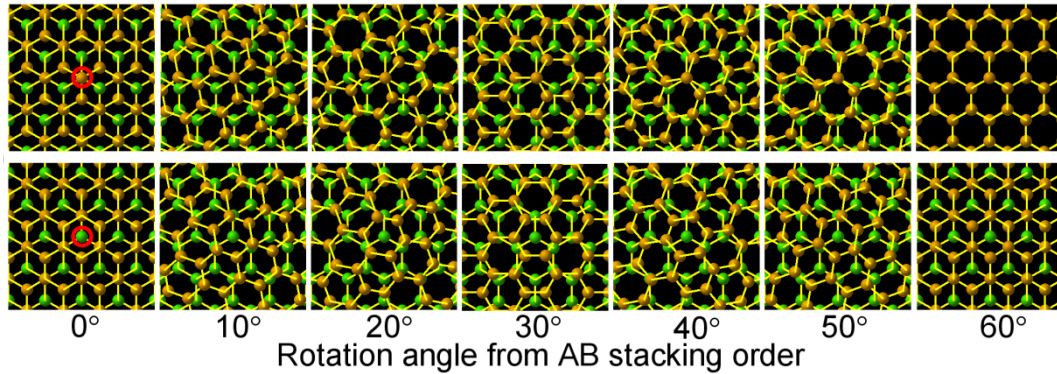
# Thermal transport in multi-layer graphene

- Motivated by the strong mechanical and thermal anisotropy observed experimentally in graphite

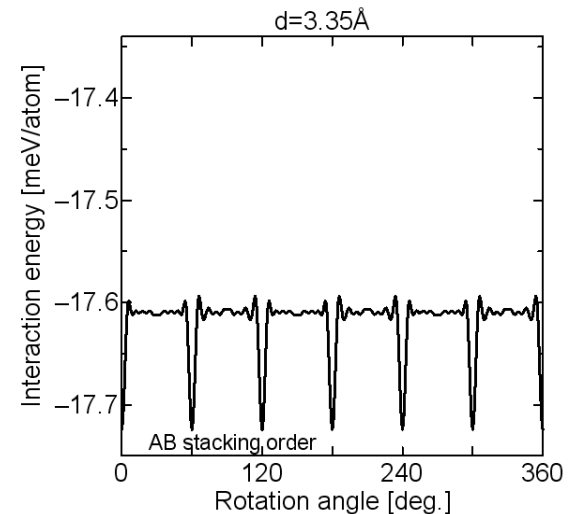
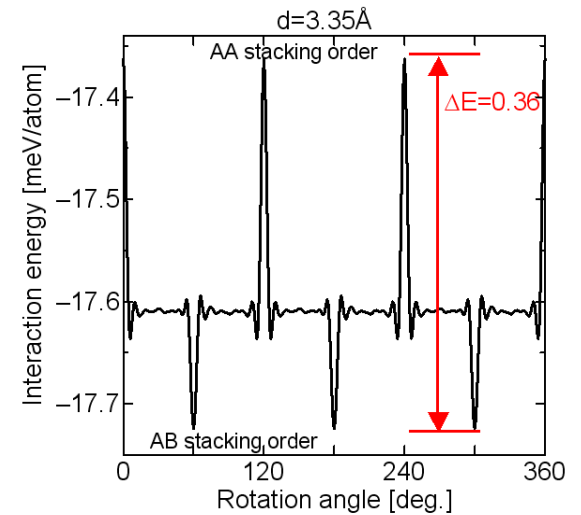
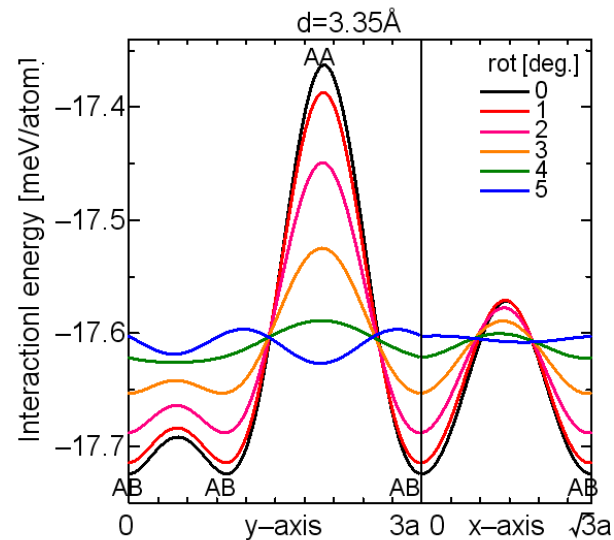
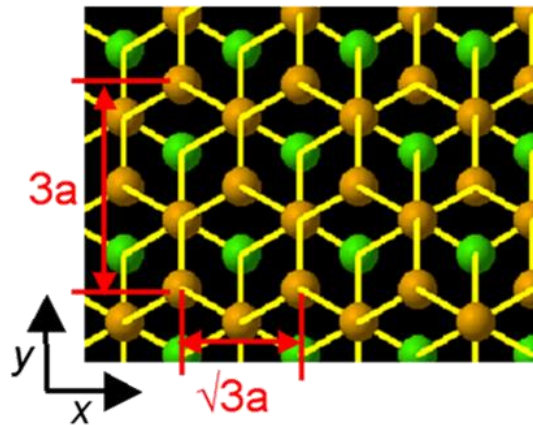


- Non-monotonic behaviour of shear stress transfer predicted as a function of temperature

# Sliding of turbostratic bilayer graphene is facile



[1]

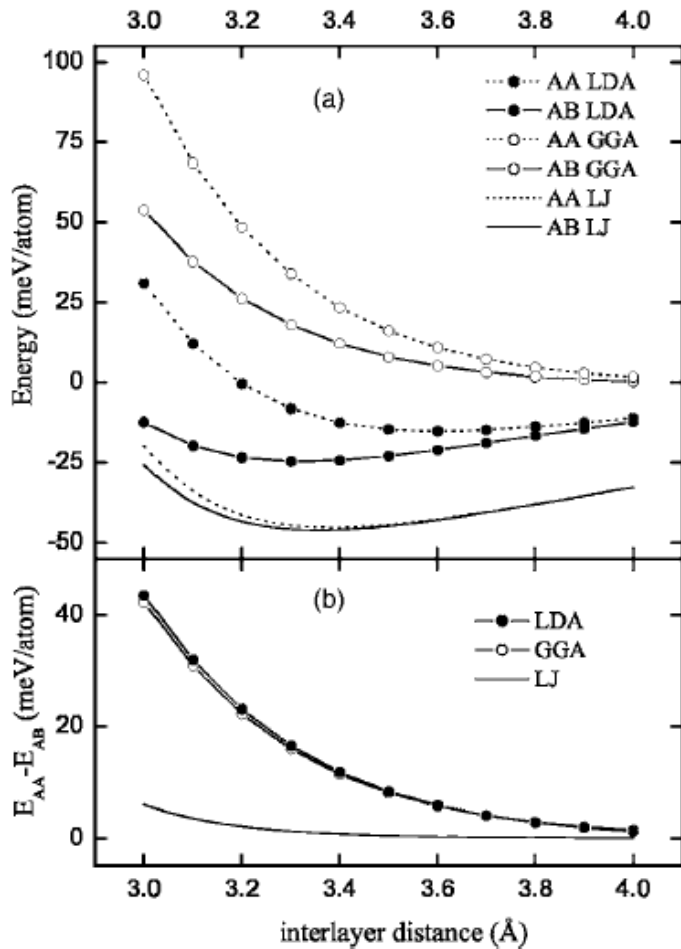


[1] Shibuta and Elliott *Chem. Phys. Lett.*, **512**, 146-150 (2011).

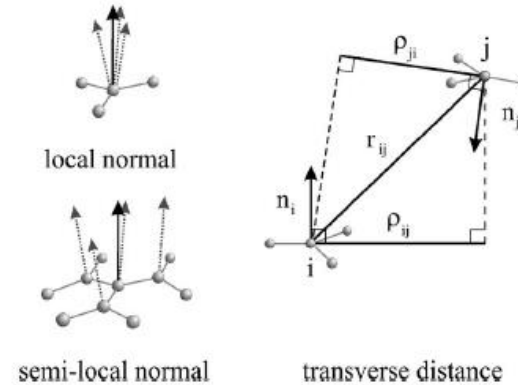
[2] Jiang et al. *J. Appl. Phys.* **113** 194304 (2013).



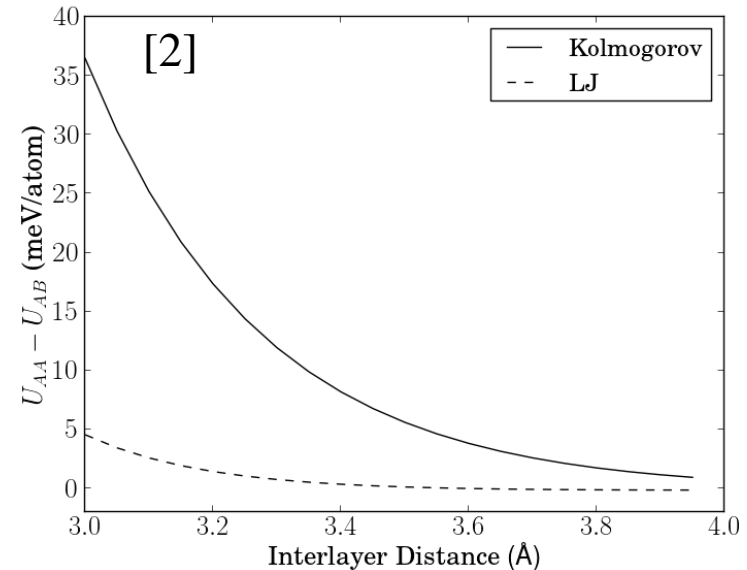
# 'Registry-dependent' interlayer potential (RDP)



[1]



$$V(r_{ij}, \mathbf{n}_i, \mathbf{n}_j) = e^{-\lambda(r_{ij}-z_0)} [C + f(\rho_{ij}) + f(\rho_{ji})] - A \left( \frac{r_{ij}}{z_0} \right)^{-6}$$



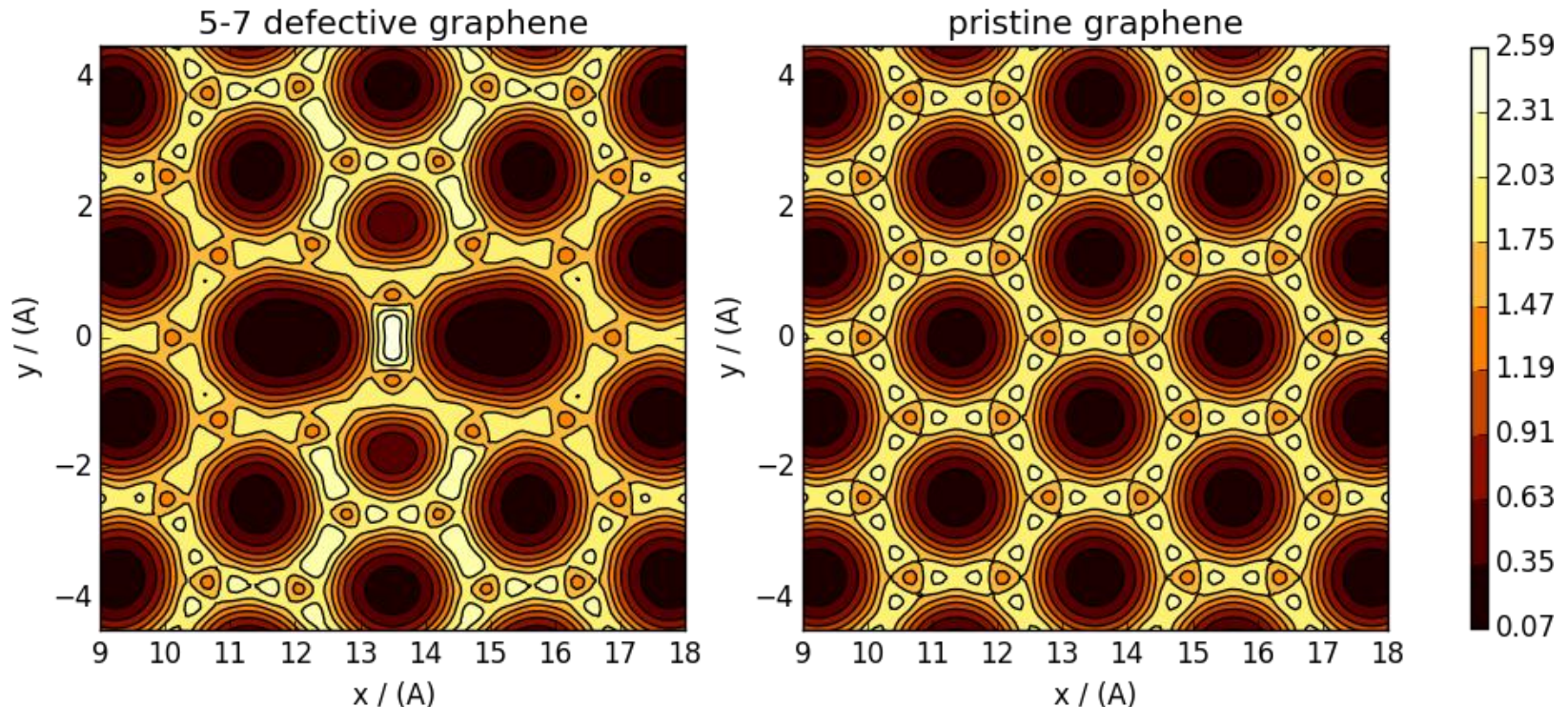
[1] Kolmogorov and Crespi *Phys. Rev. B*, **71**, 235415 (2005).

[2] Fowler and Elliott, unpublished (2015).



# Motivation for the use of RDP

- Anisotropy of valence electron density between intra/inter-plane atoms may strongly affect thermal transport



[calculated using PBE (600 eV cut off) with Tkatchenko-Scheffler dispersion correction]

# Summary and Conclusions

- *Thermal boundary resistance (TBR) of uncrosslinked CNT-PE interface is LARGE – radial heat transfer about one order of magnitude slower than through equivalent volume of polymer*
- *This is mainly due to the Kapitza effect from weak (vdW) phonon coupling between stiff CNT and flexible PE matrix*
- *Covalent crosslinking can significantly decrease TBR, and effect appears to be linear with crosslink density for low densities. Only a relatively weak (ca. 20%) dependence on covalent bond strength*
- *Preliminary results indicate that crosslink densities between 5-10% are required to achieve perfect interfacial transfer*
- *Presence of transcrystalline polymer layer appears to have detrimental effect on TBR, and reduces effectiveness of crosslinking*

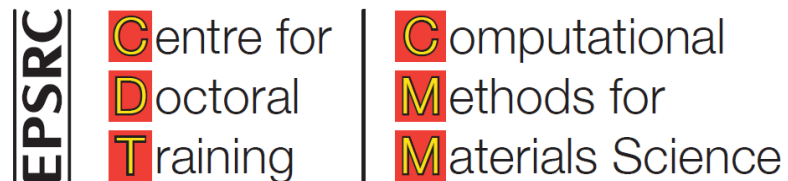


# Thanks and acknowledgements

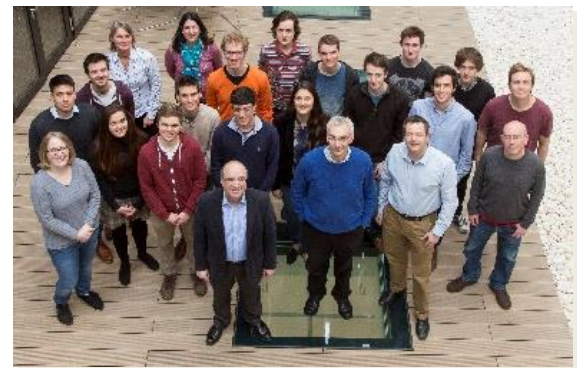
- Japan Society for Promotion of Science (JSPS) for supporting Long Term Invitation Fellowship



- University of Tokyo and Prof Junichiro Shiomi
- MPhil Project students: Jason Tabachnik (2013-14) and Michelle Kelley (2014-15)
- PhD student: Andrew Fowler (EPSRC CDT in Computational Methods for Materials Science)







## An EPSRC Centre for Doctoral Training on Computational Methods for Materials Science

**At least 12 MPhil + PhD Studentships in the University of Cambridge in the Depts of  
Physics, Chemistry, Materials, Engineering & Chemical Engineering**

Applications are invited for a four-year MPhil + PhD Centre for Doctoral Training (CDT) Programme at the University of Cambridge which will train students in the development and application of computational methods for predicting, understanding and enhancing properties of materials.

For further enquiries, email the CDT Director, Prof. M Payne (Physics): [mcp1@cam.ac.uk](mailto:mcp1@cam.ac.uk), or one of the Deputy Directors, Dr J Elliott (Materials Science) [jae1001@cam.ac.uk](mailto:jae1001@cam.ac.uk) or Dr N Nikiforakis (Scientific Computing): [nn10005@cam.ac.uk](mailto:nn10005@cam.ac.uk)

