A Computational and Experimental Study of the Electrical and Thermal Properties of Hybrid Nanocomposites based on Carbon Nanotubes and Graphite Nanoplatelets

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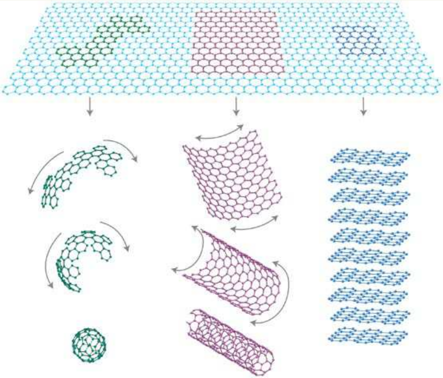
Outline

What are Carbon Nanotube (CNT) and Graphite Nanoplatelet (GNP)?

Graphene

One-atom-thick planar sheets of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice.(Wikipedia)



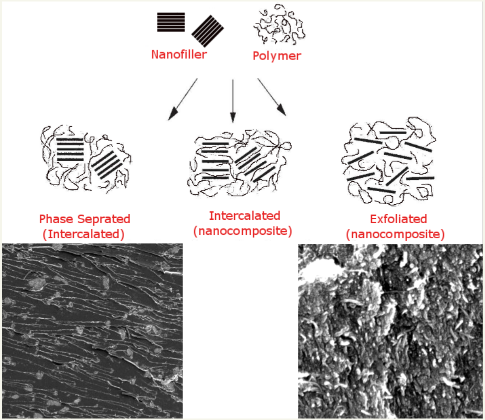
Geim et al, 2007

http://www.youtube.com/watch?v=i9dqO7aTieE&playnext=1&list=PLDDB0CB7A0C19C93A&feature=results_main http://www.youtube.com/watch?v=W-9RoQPBFFE

What is a polymer nanocomposite?

Nanocomposites

Composite in which at least one of the phase domains has at least one dimension of the order of nanometers. (IUPAC)



M. Tehrani, M. Safdari, M.S. Al-Haik "Nanocharacterization of creep behavior of multiwall carbon nanotubes/epoxy nanocomposite", International Journal of Plasticity, 2011

Why polymer nanocomposite (PNC) are important?

Size effect

- From $1\mu m^3$ to $1nm^3$
  - Number: $\times 10^9$
  - Interface surface: $\times 10^6$
  - particle/particle distance: $\times 10^{-3}$
- Increased interface volume: e.g. for only $1\%vol$ of nanospheres, $V_{interface}/V_{polymer} \simeq 63\%vol$ (Winey et al, 2007)
- Quantum confinement effects: Electrical and Optical properties

Advantages

- (1–5%) of nanoparticles, equivalent to (15–40%) of traditional fillers
- Easier processing
- Reduced weight/cost
- Unique properties not normally possible with traditional fillers
  - Opacity
  - Reduced permeability
  - Self-passivation
  - Enhanced thermal/electrical conductivity
- Overcoming traditionally antagonistic combinations of properties
- Applications: high performance multifunctional materials

Why nanofillers are important?

	Approximate Shape	Smallest Dimension (nm)	Aspect Ratio	Elastic Modulus (GPa)	Electrical Conductivity (S/cm)	Thermal Conductivity (W/mK)	Commercial Applications
Traditional Fillers							
Carbon Black	agglomerate of spheres	10-100	1-5	...	10-100	0.1-0.4	tires, hoses, shoes, elastomers
Carbon fiber	rods	5,000-20,000	10-50	300-800	0.1-10	100-1000	aerospace, marine, sporting, medical
Carbon graphite	plate	250-500	15-50	500-600	1-10	100-500	gaskets, seals
E-glass	rod	10,000-20,000	20-30	75	...	...	marine, automotive, filtration
Mineral: $CaCO_3$	sphere platelet	45-70 600-4,000	≈ 1 1-30	35	...	3-5	paper, paint, rubber, plastics
Mineral: silica	agglomerate of spheres	8,000-30,000	5-10	30-200	...	1-10	reinforced plastics, thermal insulator, paint, rubber reinforcing agent
Mineral:talc,china clay	platelet	5,000-20,000	5-10	1-70	...	1-10	paper, consumer goods, construction
Nanoscale Fillers							
Carbon nanofiber	rod	50-100	50-200	500	700-1000	10-20	hoses, aerospace, ESD/EMI shielding, adhesives
SWCNT	rod	0.6-1.8	100-10,000	1500	1000-10,000	Up to 3000	filters, ESD/EMI shielding
Aluminosilicate nanoclay	plate	1-10	50-1000	200-250	...	1-10	automotive, packaging, sporting, tires, aerospace
Nano-TiO_2	sphere	10-40	≈ 1	230,000	$10^{-11} - 10^{-12}$	12	photocatalysis, gas sensors, paint
Nano-Al_2O_3	sphere	300	≈ 1	50	10-14	20-30	seal rings, furnace liner tubes, gas laser tubes, wear pads

Winey et al, 2007

Are CNTs and GNPs comparable?

Property	Single-walled CNTs	Carbon Nanofibers	GNPs	Copper
Specific Gravity (g/cm^3)	0.8	$1.8(AG)^a - 2.1(HT)^b$	$1.8 - 2.2$	8.9
Elastic Modulus (TPa)	≈ 1 (axial direction)	$0.4(AG) - 0.6(HT)$	≈ 1 (in-plane)	0.117
Strength (GPa)	$50 - 500$	$2.7(AG) - 7.0(HT)$	$\approx 100 - 400$	220
Resistivity ($\mu\Omega cm$)	$5 - 50$	$55(HT) - 1000(AG)$	50 (in-plane)	1.68
Thermal Conductivity ($Wm^{-1}K^{-1}$)	Up to $2,900$ (estimated)	$20(AG) - 1950(HT)$	$5,300$ (in-plane) $6 - 30$ (c-axis)	401
Magnetic Susceptibility (emu/g)	22×10^6 (radial) 0.5×10^6 (axial)	N/A	22×10^6 ($\perp$ to plane) 0.5×10^6 ($\parallel$ to plane)	6.4×10^6
Thermal Expansion (K^{-1})	Negligible in the axial direction	-1×10^{-6} (HT: axial)	-1×10^{-6} (in-plane) 29×10^{-6} (c-axis)	3.9×10^{-3}
Thermal Stability ($°C$)	> 700 (in air) 2800 (in vacuum)	$450 - 650$ (in air)	$450 - 650$ (in air)	$165 - 230$ (in air) (nanoparticles)
Specific Surface Area (m^2/g)	Typically $10 - 200$ Up to $1,300$	$10 - 60$	Typically $100 - 1,000$ up to $> 2,600$	Typically $40 - 60$ (nanoparticles)

[a] AG: as grown

[b] HT: Heat treated (graphitic)

Jang et al, 2008

What are the research objectives of this dissertation?

Research Objectives

For electrical/thermal properties of CNT and GNP-based PNCs:

- Develop quantitative/qualitative models.
- Compare proposed models with literature and discuss discrepancies.
- Extend to hybrid CNTs/GNPs/Polymer nanocomposites.
- Study the advantages of the hybrid nanocomposite.
- Validate proposed models with the in-house experimental results.

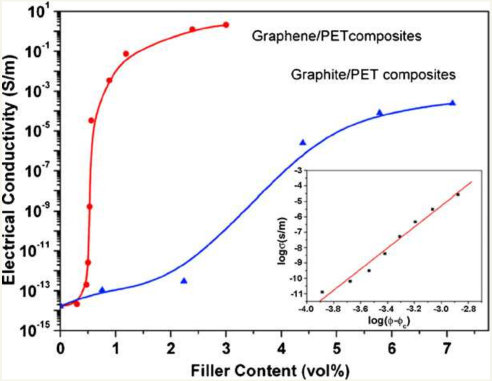
Electrical properties of CNTs/GNPs based PNCs

What has been done?

How does addition of CNTs or GNPs change the electrical conductivity of PNCs?

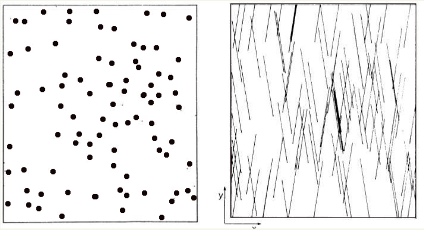
Experimental observations

- Sharp increase in the electrical conductivity in a narrow volume fraction
- S-shaped curve: Classic percolation law
- Narrow range of volume fractions called percolation threshold (ϕ_c)
- Very low ϕ_c compared to carbon black, carbon fibers and $\cdots$



Kuilia et al, 2010

Any model developed to predict the percolation threshold in PNCs?



Object Percolation

- 1974: Pike et al. ⇒ Statistical Monte Carlo methods
- 1983: Balberg et al. (Sticks)
- Some Key Publications:
  - 1995: Garboczi et al. (Ellipsoids)
  - 2004: Grujicic et al. (CNTs: Low percolation Threshold)
  - 2005: Du et al. (CNTs: Alignment effect)
  - 2007: Li et al. (CNTs: Dispersion state)
  - 2007: Li et al. (GNPs: Low Percolation Threshold)
  - 2007: Berhan et al. (Fibers: Waviness)
  - 2010: Asiaei et al. (CNTs: Geometrical Distribution)

Is there any model to quantify the electrical conductivity of PNCs?

Classical Percolation Law

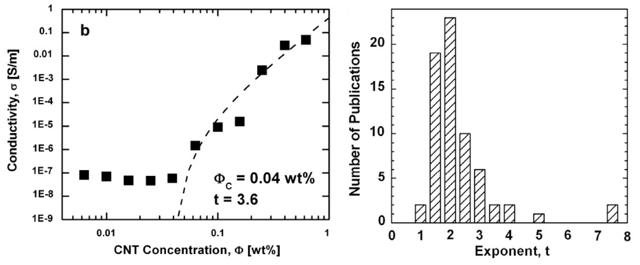
(Stauffer et al,1994): Electrical conductivity can be described by

$$\sigma \propto (\phi - \phi_c)^t \qquad (1)$$

ϕ: filler volume fraction ϕ_c: critical percolation threshold
t: conductivity exponent, for a regular 3D system $t \approx 1.6 - 2$, for complicated systems 3.0 or more (Bauhofer et al,2009).

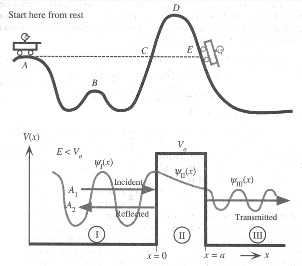
Limitations

- Narrow applicability range
- Physically interconnected network (No tunneling)
- Only applicable to large particles (Agglomerates)



Bauhofer et al, 2009

Is there any model to quantify tunneling the electrical conductivity between a pair of nanoparticles?



Kasap, 2006

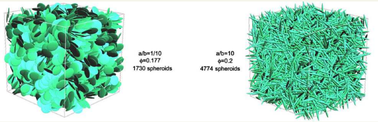
Ambrosetti et al 2010

- Switching between percolation/tunneling mechanism governed by parameter ϵ/D where ϵ is tunneling distance, D is particle diameter.
- Later in 2010, electrical conductivity a pair of prolate and oblate conductive nanoparticles governed by

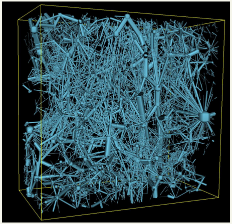
$$\sigma_{ij} = \sigma_{pre} \exp(-\frac{2\delta_{ij}}{\epsilon}) \tag{2}$$

δ_{ij}: shortest distance between two particle surfaces
σ_{pre}: constant exponential prefactor

How conductive-pair model can be extended to PNCs?



Ambrosetti, 2010



Global Tunneling Network (GTN)

Using equation 3:

$$\sigma_{ij} = \sigma_{pre} \exp(-\frac{2\delta_{ij}}{\epsilon})$$

Constitute a global tunneling network (GTN) and calculate the effective electrical conductivity.
GTN method is computationally expensive
Ambrosetti 2010: GTN results can be reproduced by Critical Path (CP) approximation method (Shklovskii,1975)(Pollak,1972)

$$\sigma_c = \sigma_0 \exp(-\frac{2\delta_c}{\epsilon}) \quad (3)$$

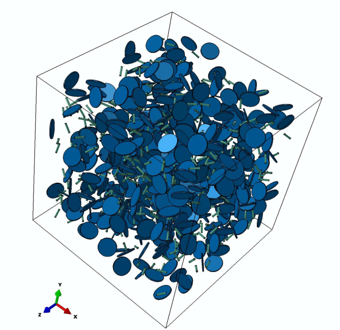
δ_c: Critical distance found through Monte-Carlo simulation

https://nf.nci.org.au/annual_reports/2005/data/project_reports/Knackstedt_M_A_h85.html

Electrical properties of CNTs/GNPs based PNCs

What has been done in this dissertation?

How does tunneling mechanism affect the percolation threshold?



Motivations

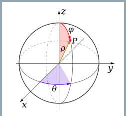
- Computation studies: Ultra low percolation threshold!
- Hardcore/Softcore debate!
- Tunneling was not confirmed for GNPs!

Propose: Monte-Carlo (MC) simulation of GNP-based PNCs

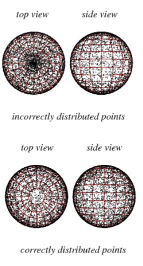
What are the simulation steps in the proposed MC code?

Random Spherical Dispersion

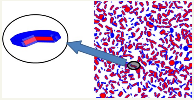
X,Y,Z : Randomly selected inside RVE



$$\begin{cases} \theta = 2\pi v \\ \varphi = Arccos(2u - 1) \end{cases} \quad (4)$$

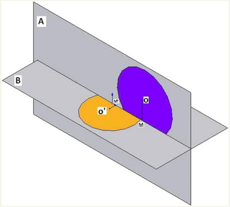


http://mathworld.wolfram.com/SpherePointPicking.html



Fast Algorithm

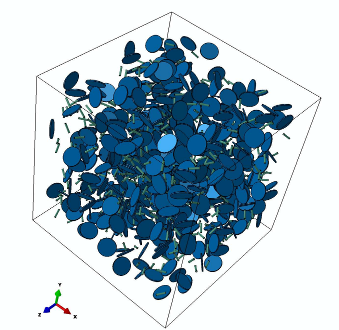
$$\begin{cases} if\ D > r + R \Rightarrow NC \\ if\ D \leq r + R \Rightarrow C \end{cases} \quad (5)$$



What are the simulation steps in the proposed MC code?

Percolation test

- Add a new particle
- Assign a new cluster number to the particle
- Check for tunneling shell interference with the neighbors
- Update the cluster number if interference was detected



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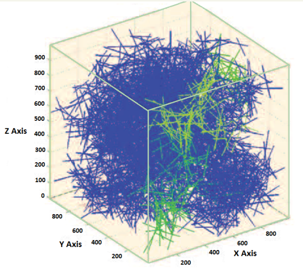
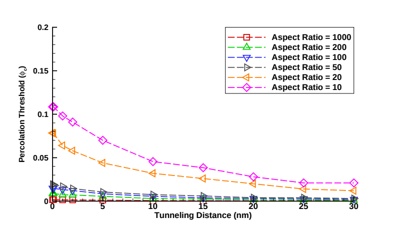
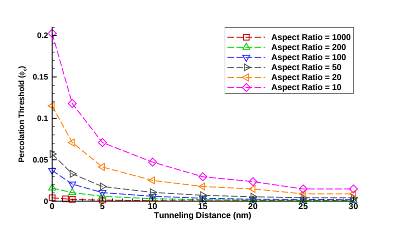


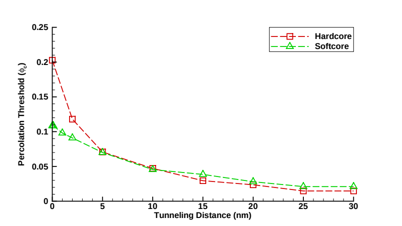
What is the effect of tunneling distance on the percolation threshold?



Softcore



Hardcore



Softcore vs. Hardcore
GNP aspect ratio = 10

M. Baniassadi, M. Safdari et al. "Incorporation of electron tunnelling phenomenon into 3D Monte Carlo simulation of electrical percolation in graphite nanoplatelet composites", Journal of physics D: Applied Physics, 2011

Is there any agreement between the simulation results and experimental observations?

Validation Study

Study Case	Aspect Ratio	d (μm)	t (nm)	Predicted Percolation Threshold (%Vol)	Exp. Percolation Threshold (%Vol)
Weng et al. 2004	600	6	10	0.668	4.6
Fukushima and Drzal 2006	1,579	15	9.5	0.294	1.13
Chen et al. 2002	5,000	50	10	0.11	0.67

Pros/Cons

- Higher percolation threshold but still low!
- Perfect GNPs
- Constant Tunneling Distance
- No agglomeration
- Fast algorithm fails for very high aspect ratio

Why MC code Ver 2.0 was needed?

MC code Ver 2.0

Features Added:

- Non-Penetration: precise algorithm (separation line method)
- Hybridization: cylinder/disk shaped nanoparticles
- Agglomeration: variable particle geometric factors
- Dispersion: improved particle dispersion technique

How the proposed MC simulation can predict the electrical conductivity of PNCs?

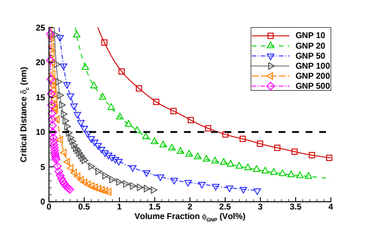
Critical Distance

From equation 3:

$$\sigma_c = \sigma_0 \exp(-\frac{2\delta_c}{\epsilon})$$

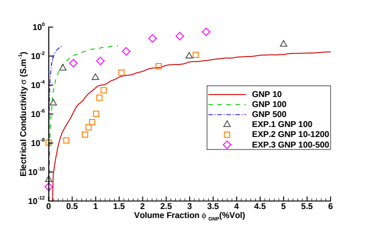
δ_c: Critical distance found through Monte Carlo simulation
Steps:

- i Generate initial structure
- ii Add penetrable shell to the species
- iii Check for percolation, if no increase shell thickness and go to *ii*, if yes go to *iv*
- iv Repeat *i-iii*, N times and find average shell thickness (t_{avg})
- v $\delta_c = 2 \times t_{avg}$

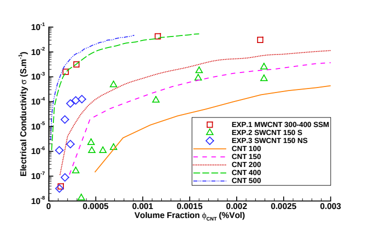


Critical Distance: GNPs

What are MC predictions for the electrical conductivity of PNCs loaded with CNTs and GNPs?



Validation study: GNPs



Validation study: CNTs

Future Work: Modeling Uncertainties

Work on assumptions:

- Perfect Geometry
- No Fragmentation, Folding, Waviness
- No Agglomeration
- Uniform Distribution

M. Safdari, M.S. Al-Haik "Electrical Conductivity of Synergistically Hybridized Nanocomposites based on Graphite Nanoplatelets (GNPs) and Carbon Nanotubes (CNTs)", Nanotechnology, 2012

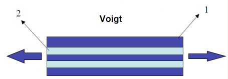
Thermal properties of CNTs/GNPs based PNCs

What has been done?

What are the upper bound and the lower bound for the properties?

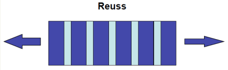
Upper Bound: Arithmetic Average or Voigt Model

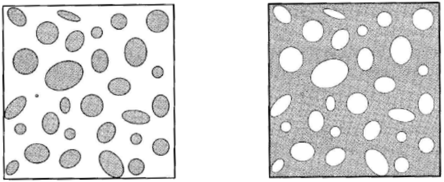
$$\sigma_e = \sum_{i=1}^{N} \phi_i \sigma_i \qquad (6)$$



Lower Bound: Harmonic Average or Reuss Model

$$\frac{1}{\sigma_e} = \sum_{i=1}^{N} \frac{\phi_i}{\sigma_i} \qquad (7)$$

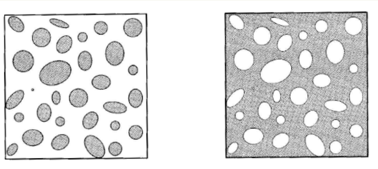




50–50 Mixture　　50–50 Mixture

Dr. Adams Lecture Notes

What are the microstructural details and how to represent them through statistical descriptor functions?



Dr. Adams Lecture Notes

Microstructural details

- Volume fractions
- Orientations/Sizes/Shapes
- Spatial distribution
- Connectivity
- Clustering
- Surface areas of interface

Which classical methods are utilized to predict the thermal conductivity of PNCs loaded with CNTs and GNPs?

Classical approaches

Other Methods:

- Empirical/Semiempirical methods (affdl,1976)
- Mean Field methods (Chen, 1992)
- Variational energy-based methods (Hori,1999)
- Asymptotic methods (Guinovart, 2005)
- Finite elements method (Shenogina, 2005)

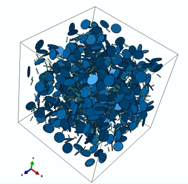
Statistical continuum methods (Torquato,2005)

Others vs Statistical

- Only for periodic microstructure (Mean Field) $\rightarrow$ Random Microstructure
- Only providing bounds (Variational Methods) $\rightarrow$ Bounds/Exact Expressions
- Only for weak contrast between the properties (Almost all) $\rightarrow$ Weak/Strong Contrast
- Slow but detailed (FEM) $\rightarrow$ Fast and Detailed

How does statistical continuum methods work?

Start with microstructure



Experimental/Computational Reconstruction

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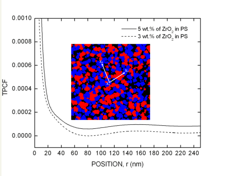
Connect microstructural details to the effective propetries



Baniassadi et al 2011

Statistical Descriptor Functions
N-point Correlation Functions
Lineal-Path Functions
Cluster Functions etc.

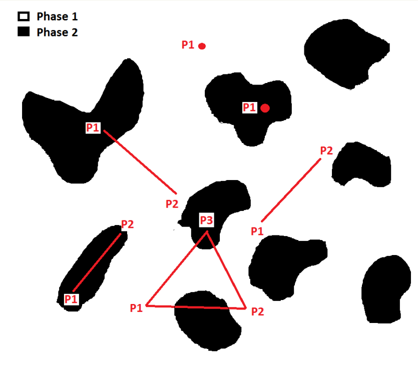
⇒

Utilize one of the available solutions:
Cluster Expansions
Exact Contrast Expansions etc.

What are the N-point correlation functions?

N-point Correlation Functions

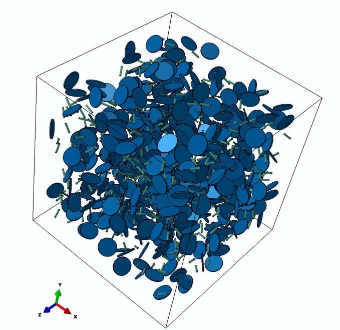
- $N = 1 \rightarrow$ information about microstructure volume fraction
- $N = 2 \rightarrow$ information about microstructure geometry
- $N = 3 \rightarrow$ more information about microstructure
- $\ldots$
- $N = \infty \rightarrow$ Full reconstruction



Thermal properties of CNT/GNP based PNCs

What has been done in this dissertation?

What is the approach for predicting the thermal conductivity of PNCs in this dissertation?

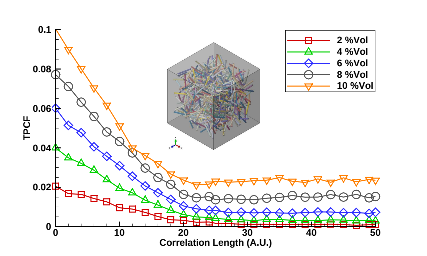


Proposed Study

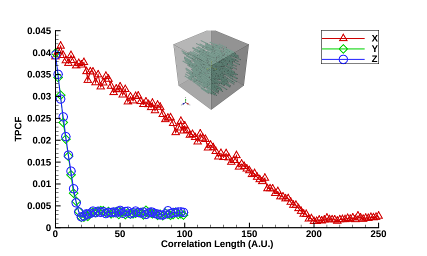
- Microstructure Generation: MC code
- Descriptor Functions: TPCFs + Approximate 3-point Correlation Functions
- Expansion: Modified Multiphase Strong-Contrast Expansion

In summary: 6 Steps

Step-1&2: What are the differences between two-point correlation functions (TPCFs) of isotropic and anisotropic microstructures?



Isotropic Tubes



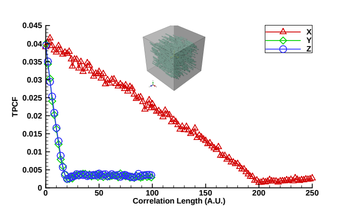
Anisotropic Tubes (Perfectly aligned in x-direction)

Step-1&2: How TPCFs describe an anisotropic microstructure?

Modified Corson approximation [1]

$$S_2^{(ij)}(r,\theta,\varphi) = a_{ij} + b_{ij}\exp(c_{ij}(\theta,\varphi)r) \quad (8)$$

$c_{ij}(\theta,\varphi)$: Found by curve fitting(θ, φ are spherical Angles)



Anisotropic

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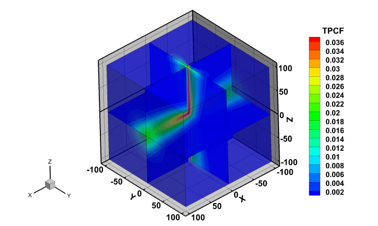


3D TPCF cut section

[1] P.B. Corson "Correlation functions for predicting properties of heterogeneous materials. II. Empirical construction of spatial correlation functions for two-phase solids", Journal of Applied Physics, 1974

Step-3: How was the strong-contrast expansion extended?

Extensions

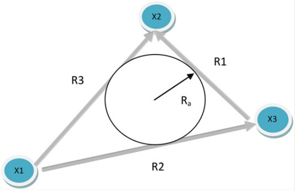
- Original 2-phase $\rightarrow$ Multi-phase
- Usually second order expansion $\rightarrow$ third-order expansion
- Three-point correlation functions $\rightarrow$ approximated from TPCFs
- Sensitive to reference phase $\rightarrow$ A novel method to reduce sensitivity

$$\left(\frac{1}{\sigma_0}\boldsymbol{\sigma_e} - \boldsymbol{I}\right)^{-1} = \frac{1}{3}\left(\frac{1}{\sum_{\alpha=1}^{3}\phi_\alpha b_{\alpha 0}} - 1\right)\boldsymbol{I} - \boldsymbol{A_2} - \boldsymbol{A_3} \tag{9}$$

$$\boldsymbol{A_2} = \frac{\sigma_0}{(\sum_{\alpha=1}^{3}\phi_\alpha b_{\alpha 0})^2}\int \sum_{\alpha=1}^{3}\sum_{\beta=1}^{3}\left(b_{0\alpha}b_{0\beta}[S_2^{(\alpha\beta)}(1,2) - S_1^{(\alpha)}(1)S_1^{(\beta)}(2)]\right) \boldsymbol{H^{(0)}(1,2)}d2 \tag{10}$$

$$\boldsymbol{A_3} = \frac{3\sigma_0}{(\sum_{\alpha=1}^{3}\phi_\alpha b_{\alpha 0})^2}\int\int\left(\sum_{\alpha=1}^{3}\sum_{\beta=1}^{3}\sum_{\gamma=1}^{3} b_{0\alpha}b_{0\beta}b_{0\gamma}S_3^{(\alpha\beta\gamma)}(1,2,3) - \frac{1}{\sum_{\alpha=1}^{3}\phi_\alpha b_{\alpha 0}}\sum_{\alpha=1}^{3}\sum_{\beta=1}^{3}\sum_{\gamma=1}^{3}\sum_{\delta=1}^{3} b_{0\alpha}b_{0\beta}b_{0\gamma}b_{0\delta}S_2^{(\alpha\beta)}(1,2)S_2^{(\gamma\delta)}(2,3)\right) \boldsymbol{H^{(0)}(1,2)H^{(0)}(2,3)}d2d3 \tag{11}$$

Step-4: How was three-point correlation functions from approximated from TPCFs?



Baniassadi et al, 2012

$$S_3^{(\alpha\beta\gamma)}(1,2,3) \approx W_1^3 \frac{S_2^{(\alpha\beta)}(1,2)S_2^{(\alpha\gamma)}(1,3)}{S_1^{(\alpha)}(1)} + W_2^3 \frac{S_2^{(\alpha\beta)}(1,2)S_2^{(\beta\gamma)}(2,3)}{S_1^{(\beta)}(2)} + W_3^3 \frac{S_2^{(\beta\gamma)}(2,3)S_2^{(\alpha\gamma)}(1,3)}{S_1^{(\gamma)}(3)} \quad (12)$$

$$W_i^3 = \frac{R_i}{\sum_{j=1}^{3} R_j} \quad , i = 1 \cdots 3 \quad (13)$$

Step-5: How did the sensitivity of multiphase third order Strong-Contrast expansion reduce?

sensitivity analysis

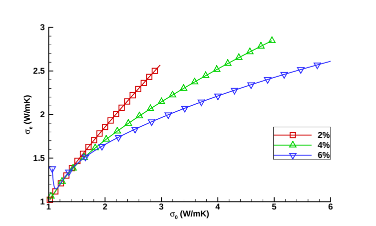
Equation 9 can be solved for $\boldsymbol{\sigma_e}$:

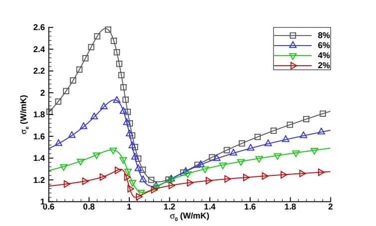
$$\boldsymbol{\sigma_e} = \sigma_0 \left(\boldsymbol{I} + \left(\frac{1}{3}\left(\frac{1}{\sum_{\alpha=1}^{3} \phi_\alpha b_{\alpha 0}} - 1\right)\boldsymbol{I} - \boldsymbol{A_2} - \boldsymbol{A_3}\right)^{-1} \right) = \boldsymbol{f}(\sigma_0, microstructure) \quad (14)$$

Thus

$$\boldsymbol{e}(\sigma_0) = \left(\boldsymbol{f}(\sigma_0) - \boldsymbol{\sigma_{true}}\right)^2 \quad (15)$$

looking for $\partial \boldsymbol{e} / \partial \sigma_0 = 0 \rightarrow$ Candidate points



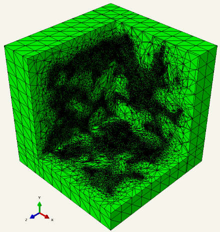


Sensitivity diagram for $\sigma_{tube}/\sigma_{matrix} = 100$

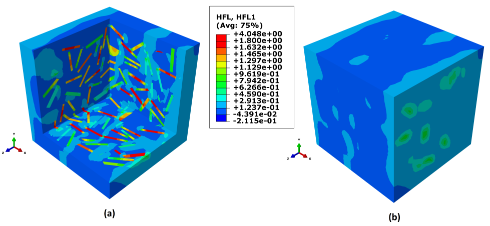
Step-6: How was the validity of the proposed method verified?

Finite Element Study

- Package: Abaqus 6.10-EF
- Pre/post-processing: Python
- Assumption: Perfect thermal bounding
- Element: DC3D4
- BC's: Constant temperature left/right sides of RVE
- Analysis: Steady-state Thermal Analysis (1 - 96 hours)
- Result: Volume averaged heat-flux vector
- Convergence: Local and global mesh refinement



Internal view of a Sample RVE



10%Vol disk-shaped inclusions (Aspect ratio= 10 and $\sigma_{disk} = 100\sigma_{matrix}$)

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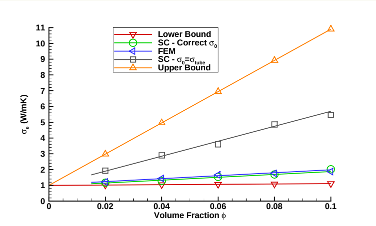
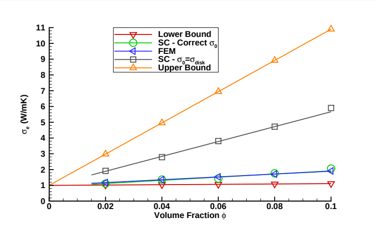
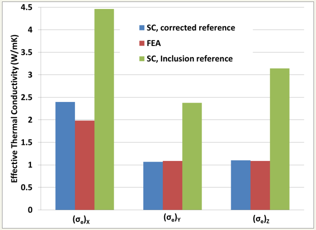
How was agreement between Modified SC and FEA?



Tube



Disk



Tube- Aligned in x-direction

What has been done experimentally?

Electrical/Thermal Properties

Enhancement for PNCs based on:

- CNTs $\cdots \checkmark$
- GNPs $\cdots \checkmark$
- CNTs + GNPs $\cdots ?$

Is there any advantage in hybridization?

Study	Electrical Conductivity	Thermal Conductivity	Description
Yu et al 2008	▼	▲	CNTs/GNPs/polymer
Lie et al 2008	▲	N/A	CNTs/GNPs/polymer
Tung et al 2009	▲	N/A	CNTs/graphene/polymer
Kim et al 2009	▲	N/A	CNTs/graphene/polymer
Yan et al 2010	▲	N/A	CNTs/graphene/polymer
Hong et al 2010	▲	N/A	CNTs/graphene/polymer
Kumar et al 2010	▲	▲	CNTs/GNPs/polymer

Proposal

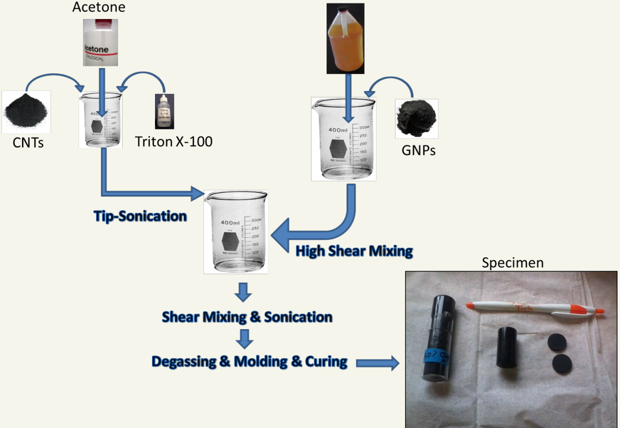
Study: hybrid CNTs/GNPs PNCs both computational + experimental
Motivations:

- Confirm synergistic effects
- Shed more light on physics
- Further validation

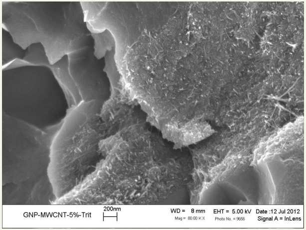
What is proposed for experimental study in this dissertation?

Experimental Study

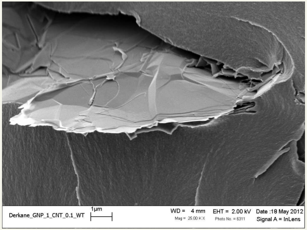
- Samples: CNT/epoxy; GNP/epoxy; CNT/GNP/epoxy
- Measurement: Electrical/Thermal Conductivity
- Microscopy/FIB/Reconstruction



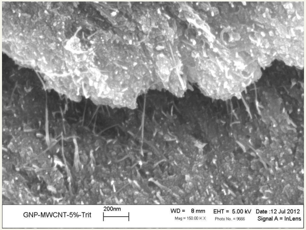
What was the preliminary observation?



CNT/epoxy

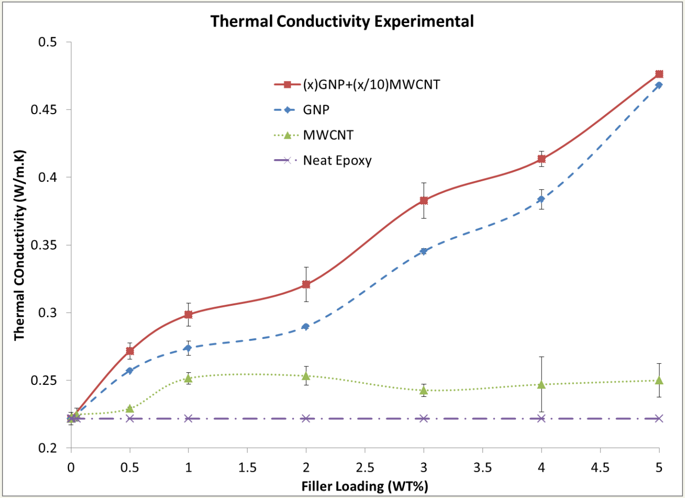


GNP/epoxy

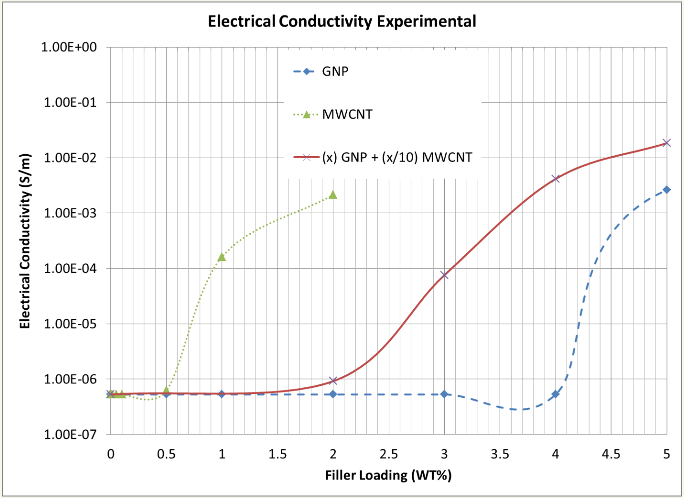


CNT/GNP/epoxy

What are thermal conductivity measurements results?



What are electrical conductivity measurements results?



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What are the next steps and their time-line?

Motivations

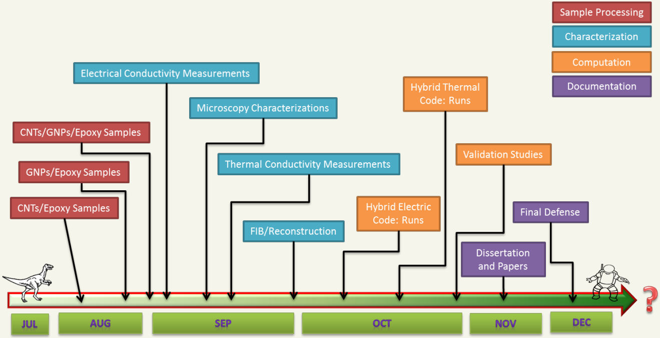
Electrical Properties
- Background
- Incorporation of Tunneling
- Quantifying Electrical Conductivity

Thermal Properties
- Background
- Quantifying Thermal Conductivity

Experimental Study
- Background
- Our Proposal

Preliminary Results

Time-Line



Journal publications

Publications:

- Safdari, M., Baniassadi, M., Garmestani, H. and Al-Haik, M. S. “A Modified Strong-Contrast Expansion for Estimating the Effective Thermal Conductivity of Multiphase Heterogeneous Materials”, *Journal of Applied Physics*, Under review
- Safdari, M. and Al-Haik, M. S. “Electrical Conductivity of Synergistically Hybridized Nanocomposites based on Graphite Nanoplatelets (GNPs) and Carbon Nanotubes (CNTs)”, *Nanotechnology*, Accepted
- Baniassadi, M., Safdari, M., Ghazavizadeh, A., Garmestani, H., Ahzi, S., Gracio, J., and Ruch, D. “Incorporation of electron tunnelling phenomenon into 3d monte carlo simulation of electrical percolation in graphite nanoplatelet composites.”, *Journal of Physics D: Applied Physics*, 44(45):455306–455313, 2011.
- Ghazavizadeh, A., Baniassadi, M., Safdari, M., Atai, A., Ahzi, S., Patlazhan, S., Gracio, J., and Ruch, D. “Evaluating the Effect of Mechanical Loading on the Electrical Percolation Threshold of Carbon Nanotube Reinforced Polymers: A 3D Monte-Carlo Study.” *Journal of Computational and Theoretical Nanoscience*, 8(10):2087–2099, 2011.
- Asiaei, S., Khatibi, A. A., Baniasadi, M., and Safdari, M. “Effects of carbon nanotubes geometrical distribution on electrical percolation of nanocomposites: A comprehensive approach.”, *Journal of Reinforced Plastics and Composites*, 29: 818-829, 2009.

Other Publications:

- Tehrani, M., Safdari, M., Yarri, A., Razavi, Z., Case, S. W., Dahmen, K., Garmestani, H., and Al-Haik, M. S. “Hybrid carbon fiber / carbon nanotubes composites for structural damping applications.”, *Carbon*, Under review
- Safdari, M. and Al-Haik, M. S. “Optimization of stress wave propagation in a multilayered elastic/viscoelastic hybrid composite based on carbon fibers/carbon nanotubes.” *Polymer Composites*, 33(2):196–206, 2012.
- Tehrani, M., Safdari, M., and Al-Haik, M. “Nanocharacterization of creep behavior of multiwall carbon nanotubes/epoxy nanocomposite.” *International Journal of Plasticity*, 27(6):887 – 901, 2011.

Thanks for your attention!

Questions??

Virginia Tech 1872

Carbon Nanotubes for Targeted Drug Delivery to Ovarian Cancer

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Workshop on Advances in Computational Mathematics and Engineering
In honor of the contributions of M. Y. Hussaini
Florida State University Sept 28-30,2012

Therapy in ovarian cancer (OVCA)

- Targeting OVCA through tumor markers or over-expressed receptors
- Expression of folate receptor alpha (FRα) or folate receptor beta (FR beta), both are 38 KDa GPI-anchored membrane glycoproteins is detected at high frequency in cancers.

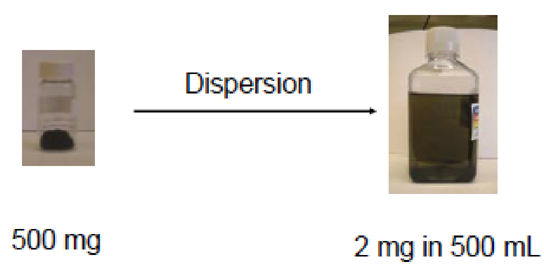
Advantages of functionalized CNTs for drug delivery

- CNTs ≤ 1 μm deliver to cells: protein, nucleic acids, drugs
- Non-immunogenic (short-term studies)
- Little toxicity (short-term studies)
- Cleared rapidly from body
- High thermal conductivity
- Hollow cylinders can introduce molecules into

internal space

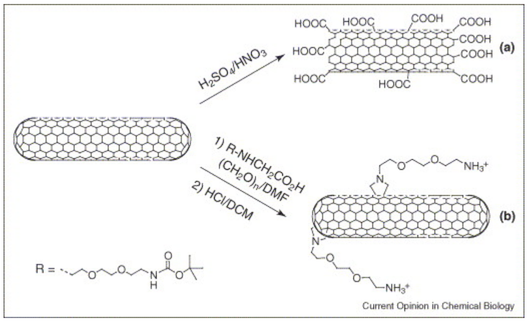
- Easy uptake

Dispersion by Functionalizing CNTs



1. Chemical conjugation
2. Adsorption (involves ultra sonication) e.g. phospholipid-polyethylene glycol (PL-PEG) ultrasonication – 1 to 2 hr

Chemical Modifications / Conjugations



Organic functionalisation of carbon nanotubes. Pristine single- or multi-walled carbon nanotubes can be **(a)** treated with acids to purify them and generate carboxylic groups at the terminal parts, or **(b)** reacted with amino acid derivatives and aldehydes to add solubilizing moieties around the external surface.

Bianco & coworkers 2005. Current Opinion in Chemical Biology 9:674-679

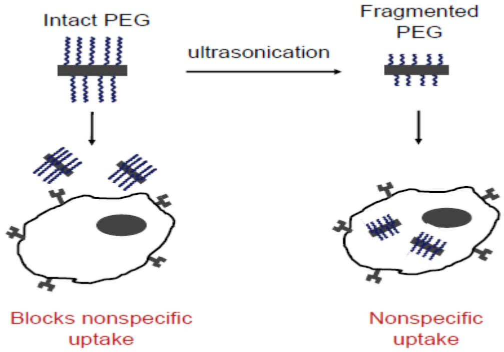
PEGylation

- Increases half-life in circulation
- Reduce non-specific uptake by cells
- Blocks non-specific binding to proteins

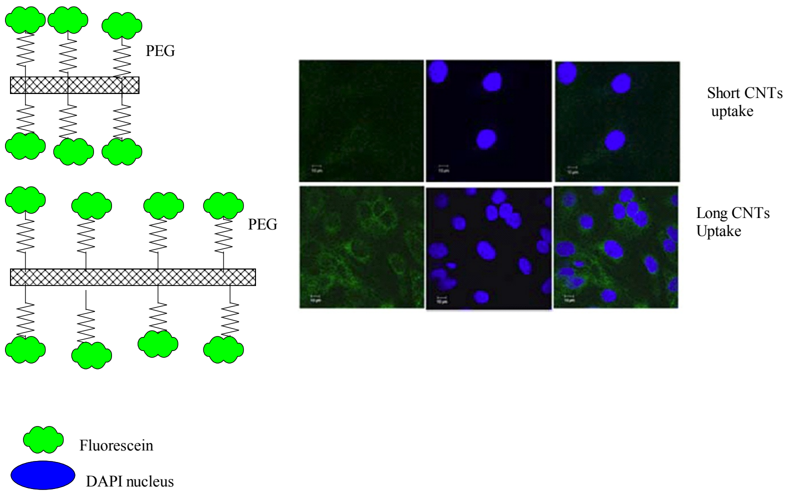
- Evaluation of cellular uptake of SWNTs functionalized by adsorbing PL-PEG led to unexpected findings:
  – PL-PEG2000 (i.e., the MW of PEG is ~2000) to SWNTs did not reduce uptake of SWNTs
  – PL-PEG5000 gave contradictory results

Hypothesis

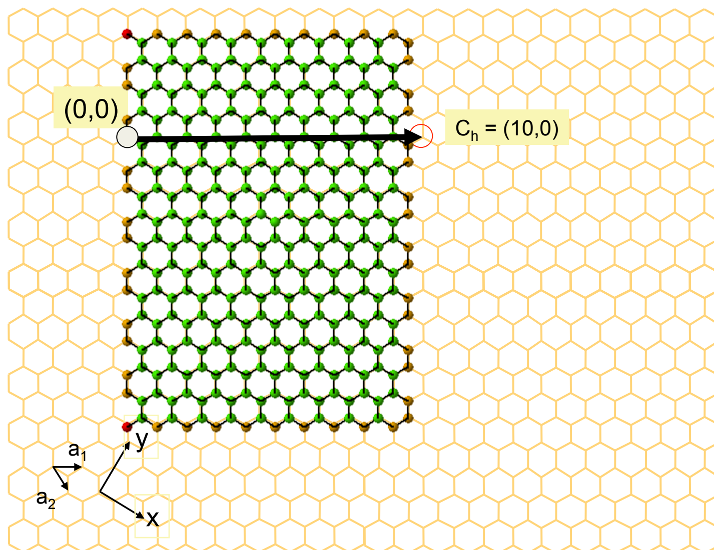
- Integrity of PEG is important to prevent nonspecific uptake of SWNTs



Evaluation of the effect of PEG/CNTs length on the uptake of SWNTs by cells

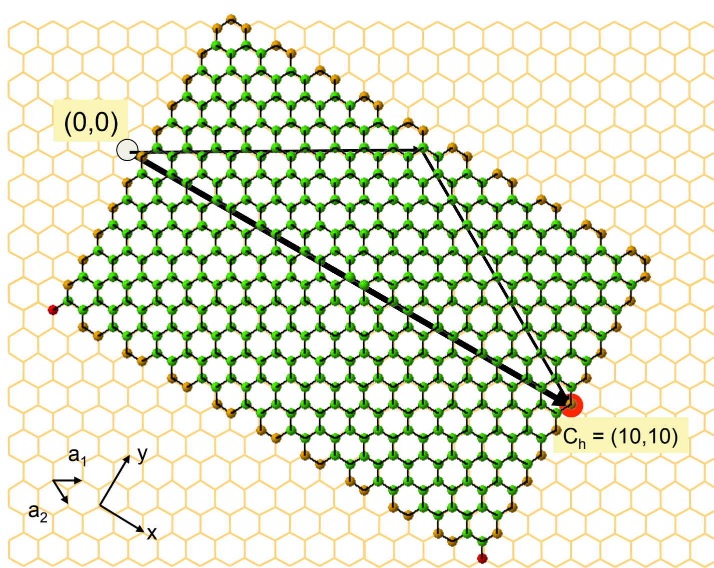


Wrapping (10,0) SWNT (zigzag)



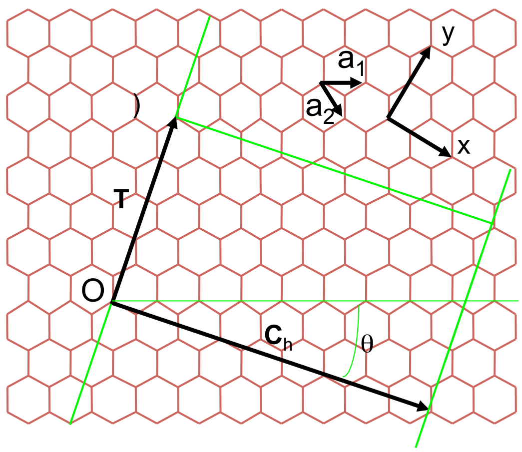
10/2/12 9

Wrapping (10,10) SWNT (armchair)



10/2/12 10

Hexagonal Lattice (Definition of Chiral Vectors)



Chiral vector:

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$$

$$\mathbf{a}_1 = (\frac{3}{2}a_{cc}, \frac{\sqrt{3}}{2}a_{cc})$$

$$\mathbf{a}_2 = (\frac{3}{2}a_{cc}, -\frac{\sqrt{3}}{2}a_{cc})$$

a_{cc} is the C–C bond length (0.142 nm).

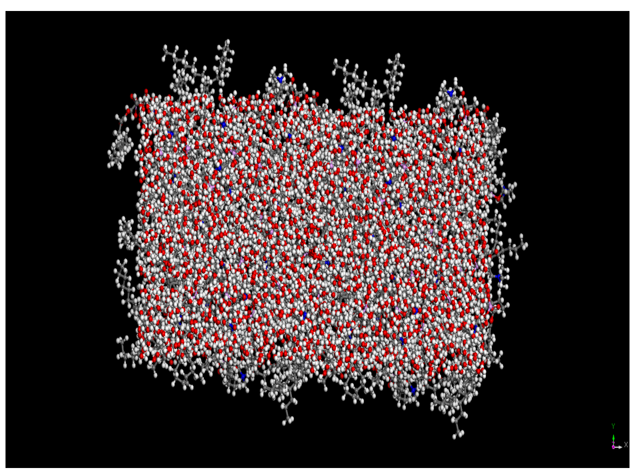
$$\theta = \arccos\left(\frac{\sqrt{3}(n+m)}{2\sqrt{n^2+m^2+nm}}\right)$$

$$D_n = \frac{\sqrt{3}}{\pi}a_{cc}\sqrt{(n^2+m^2+nm)}$$

10/2/12 11

The Membrane

72 dimyristoyl-sn-glycerophosphatidylcholine (DMPC) lipids, -a common membrane and 2716 water molecules making an overall 17,796 atoms structure.



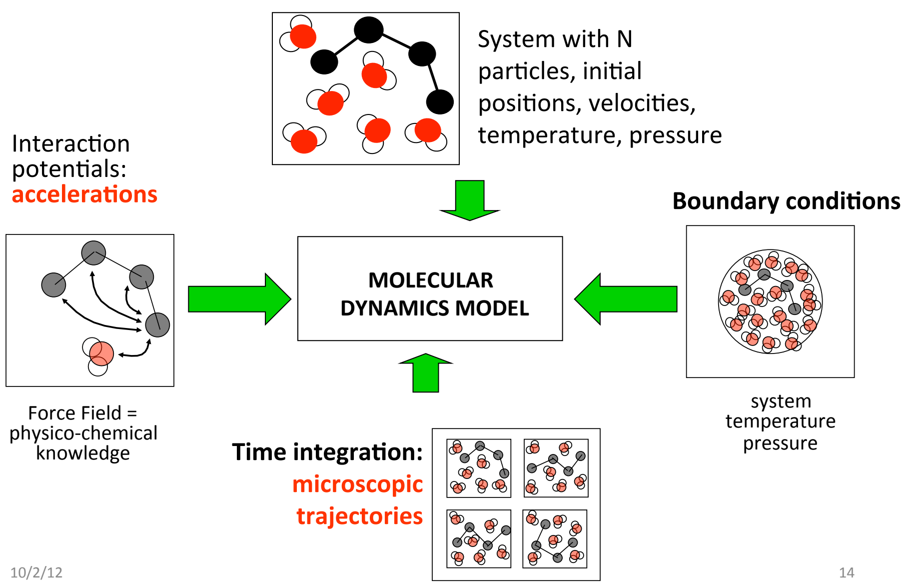
10/2/12 12

The CNTs

		H	C	Diameter (nm)	Length (nm)	Chiral Angle θ°
(10,0) NT-	short	40	600	0.783	6.5541	0.00
	long		1280		13.472	
(10,5) NT	short	50	600	1.036	5.2281	19.11
	long		1300		10.972	
(10,7) NT	short	54	600	1.158	4.8061	24.18
	long		1308		10.212	
(10,10) NT-	short	60	600	1.356	4.1278	30.00
	long		1320		8.932	

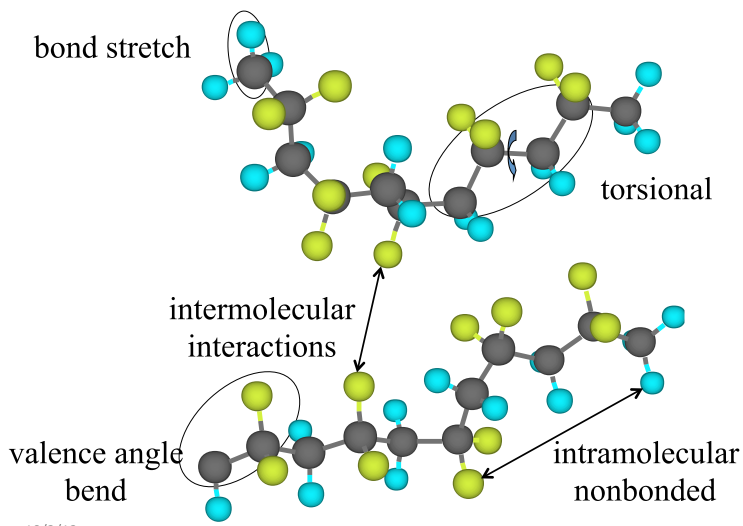
10/2/12 13

Molecular Dynamics Simulation Basics

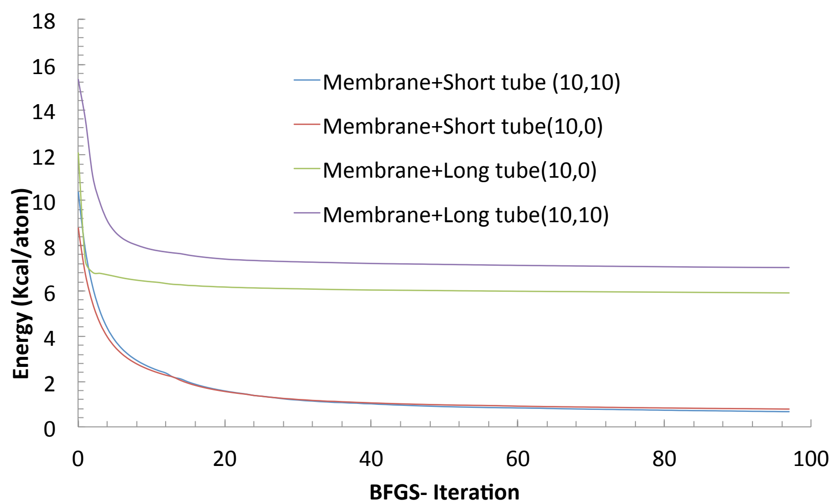


10/2/12 14

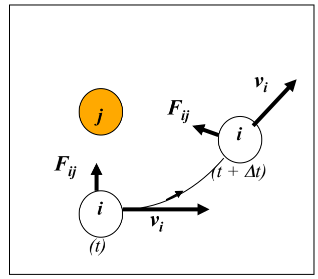
The Force Field: CHARMM27



Numerical Minimization of PE



Generating Trajectory



Newton Eqn:

$$\vec{F}_{ij} = -\frac{\partial \phi_{ij}}{\partial r_{ij}}\hat{r}_{ij} \qquad \sum_j \vec{F}_{ij} = m_i \frac{d\vec{v}_i}{dt}$$

Updated Position:

$$\vec{r}_i(t+\Delta t) = \vec{r}_i(t) + (\Delta t)\vec{v}_i(t) + \frac{1}{2}(\Delta t)^2 \frac{\vec{F}_i(t)}{m_i}$$

Updated Velocity:

$$\vec{v}_i\left(t+\frac{\Delta t}{2}\right) = \vec{v}_i(t) + \frac{1}{2}(\Delta t)\frac{\vec{F}_i(t)}{m_i}$$

$$\vec{v}_i(t+\Delta t) = \vec{v}_i\left(t+\frac{\Delta t}{2}\right) + \frac{1}{2}(\Delta t)\frac{F_i(t+\Delta t)}{m_i}$$

Controlling Thermodynamic Variables T and P

- Statistical ensembles connect microscopic to macroscopic/ thermodynamic
- NVE (microcanonical)
- NVT (Canonical)
- NPT (Isothermal-isobaric)

$$V = 1/M * \sum_{i=1}^{M} V_i$$

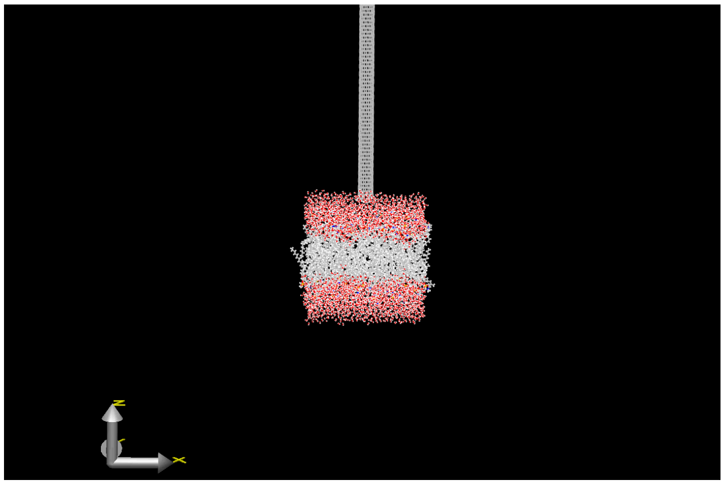
- Thermostats, barostats, etc., allow one to choose appropriate ensembles.
- Nose-Hoover thermostat is used for the temperature control

$$T_i = \frac{1}{3Nk_B}\sum_{i=1}^{N} m_i v_i^2$$

- Berendsen barostat maintain a constant desired pressure in the periodic box.

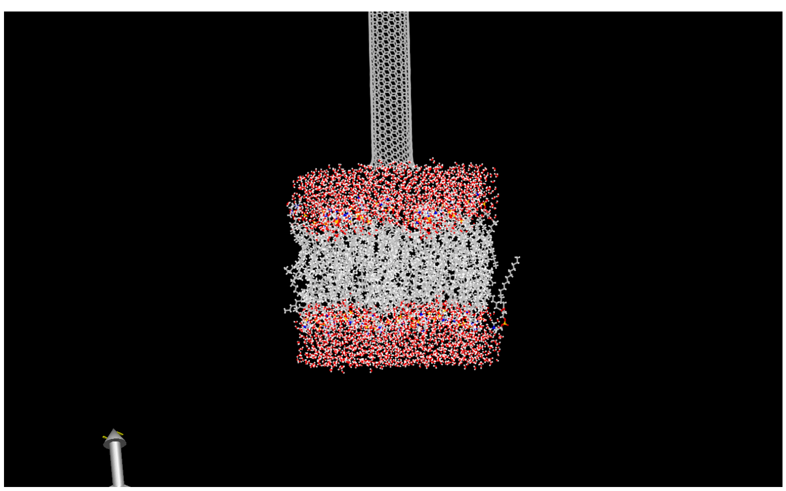
$$p_i = \frac{2}{3V}\left[\frac{1}{2}\sum_{i=1}^{N} m_i v_i^2 - \frac{1}{2}\sum_{i=1}^{N} r_i \nabla U(r_i)\right]$$

MD 10-0



10/2/12 19

MD10-10



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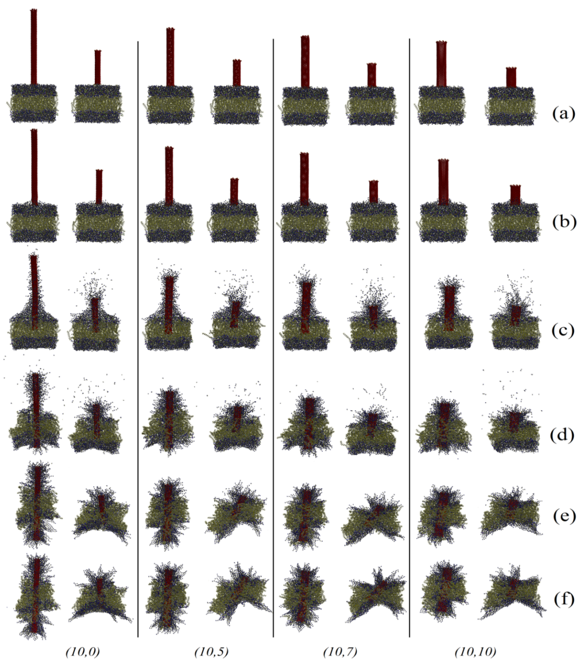
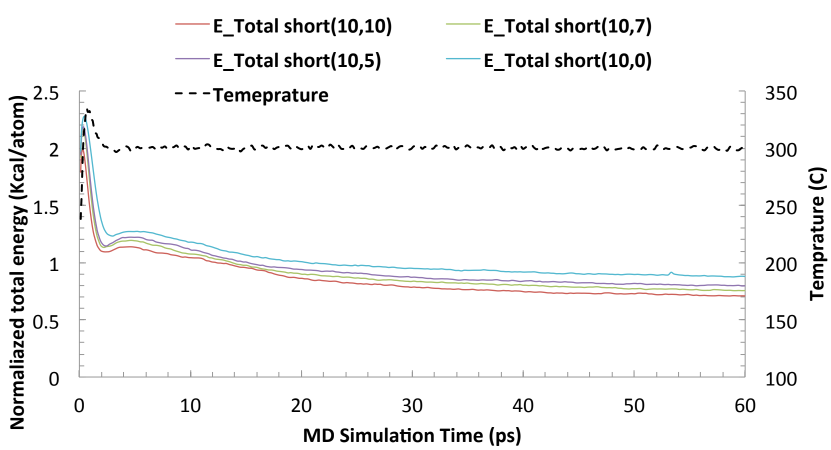
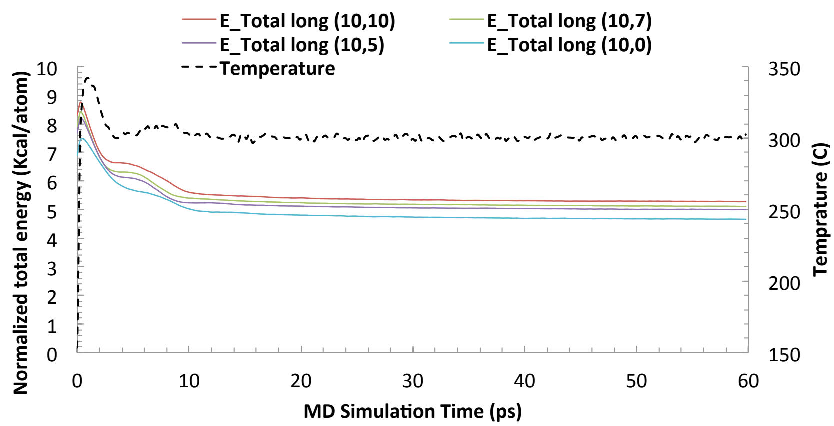


TINKER-MD
60 ps

(a) Initial configuration
(b) after 0.4 ps
(c) after 4 ps
(d) after 10 ps
(e) after 30 ps
(f) after 60 ps

Effect of the Aspect Ratio



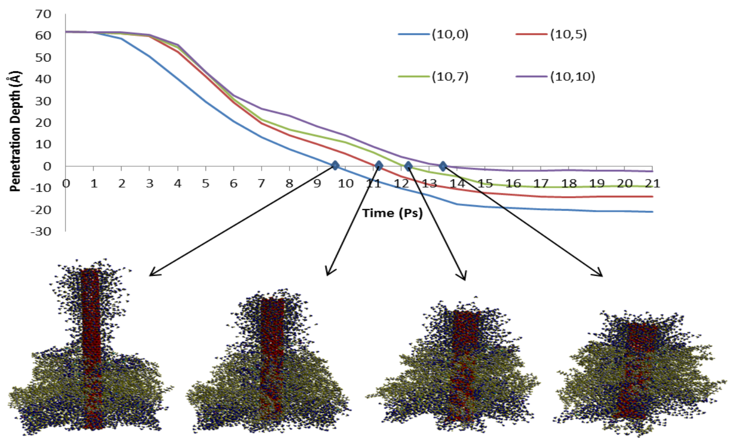


Finding

- Holding the chirality fixed, longer nanotubes find their ways through the membrane faster with less rotation from the vertical position.

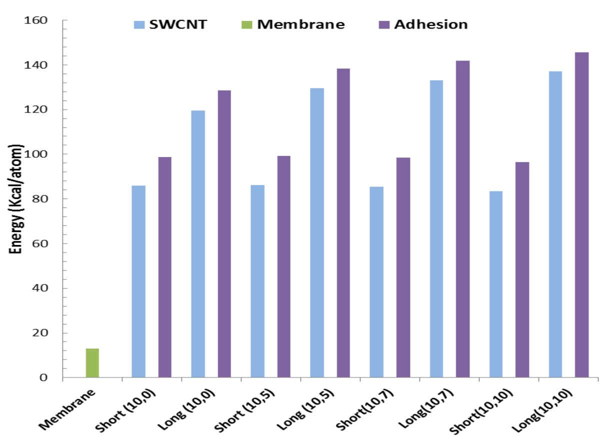
- On the contrary, tubes with length shorter than thickness of membrane (i.e.~ 60 Å) are more likely to rotate in the membrane while trafficking via endocytosis mechanism.

Effect of Chirality



Molecular dynamic evolution of the z-coordinate of bottommost carbon atom in different chiralities

Adhesion



$$\Delta E = E_{Total} - (E_{CNT} + E_M)$$

Conclusions

- At earliest time the mechanism of interaction between the SWCNT and the membrane is pure penetration. As time evolves penetration is accompanied by endocytosis and almost halfway through 60 ps, endocytosis becomes the dominant form of interaction.
- CNTs with length shorter than the thickness of the membrane- undergo significant rotation during the endocytosis stage.
- Lower chirality (higher aspect ratio) assisted the SWCNT to cross through the membrane faster.
- As lesser of the SWCNT energy was consumed to establish adhesion with the membrane it was capable of translocating through the membrane from the other side faster than the other nanotubes

Publications

NANO LETTERS

R. Zeineldin , M. Al-Haik and Laurie G. Hudson," Role of Polyethylene Glycol Integrity in Specific Receptor Targeting of Carbon Nanotubes to Cancer Cells, " Nano Letters, 2009, 9 (2), pp 751–757.

Langmuir

A. Alipour Skandani , R. Zeineldin , and M. Al-Haik ," Effect of Chirality and Length on the Penetrability of Single-Walled Carbon Nanotubes into Lipid Bilayer Cell Membranes," Langmuir, 2012, 28 (20), pp 7872–7879