van der Waals - London Dispersion Interactions For Metallic and Semiconducting Carbon Nanotubes From ab initio Unixial Optical Properties

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2. DuPont Company, Central Research & Development, Wilmington, DE U.S.A.

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Carbon Nanotubes

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R. F. Rajter, R. Podgornik, V. A. Parsegian, R. H. French, W. Y. Ching, **Phys. Rev. B** 76, 045417 (2007).
R. F. Rajter and R. H. French, J**. Phys.: Conf. Ser**. 94, 012001, (2008).
R. F. Rajter, R. H. French, R. Podgornik, W. Y. Ching, V. A. Parsegian, **J. Appl. Phys**. 104, 053513 (2008).

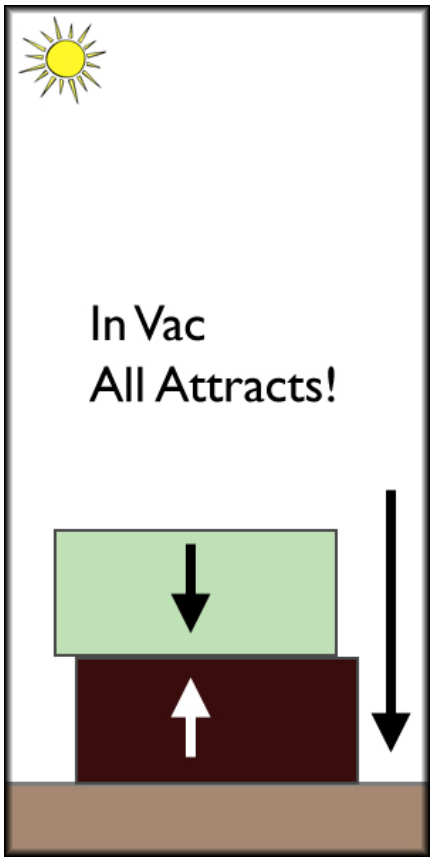
Datamining I: R. F. Rajter, W. Y. Ching, R. H. French
Datamining II:R. F. Rajter, R. H. French, R. Podgornik, V. A. Parsegian, and W.Y. Ching
End User: R. F. Rajter and R. H. French, International Journal of Materials Research

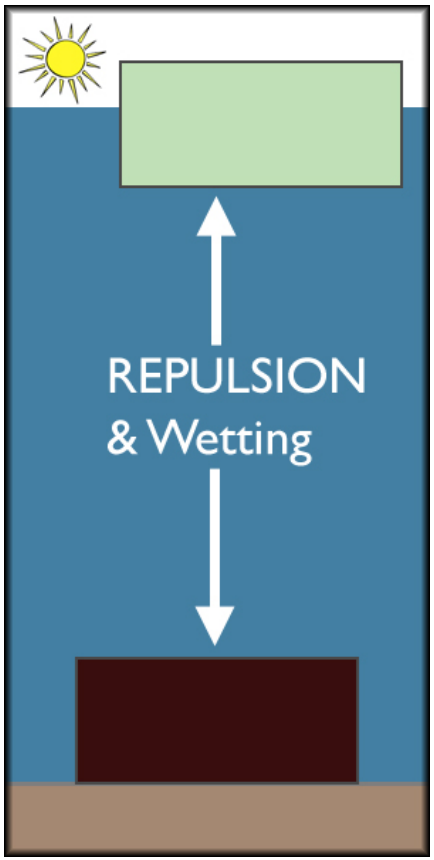
Optical Contrast Visually – Simple Attract/Repulsion

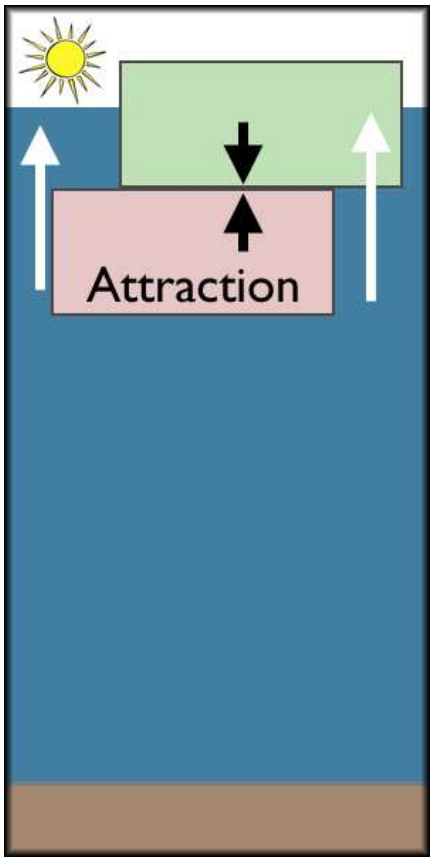
Basic Attractive/Repulsive vdW-Ld Interactions Mirror Buoyancy

Density ~ Dielectric/Optical Property Contrast or Polarizability

Darker Colors Represent Higher Density/Polarizability And Vice Versa







Introduction: Assembling Nanoscale Devices

CNT Processing And Assembly Technologies

- **Separation** By Metallic vs. Semiconducting,
- **Sorting** By Chirality
- **Placement** Of CNTs
- **Alignment** Of CNTs

Can vdW-Ld Interactions Be Used For CNT Processing?

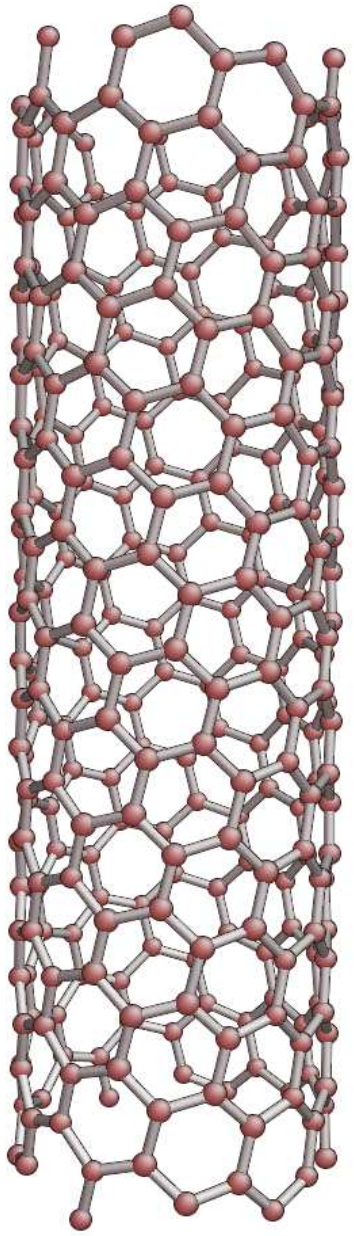
- London Dispersion Interactions: Universal, Long Range

ab Initio Optical Properties Of CNTs

- Opens The vdW-Ld Door For Previously Unsolvable Systems

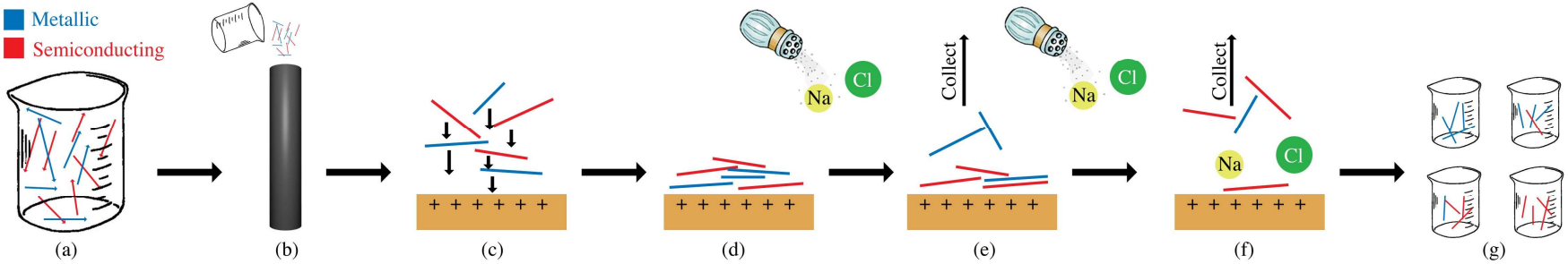
Solid Cylinder vdW-Ld Formulations

- vdW-Ld For Optical & Morphological Anisotropy



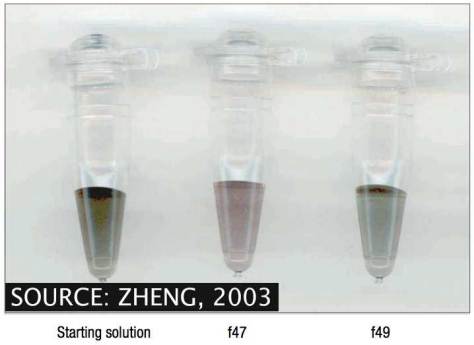
Working Separation Example: Zheng Anion IEC Experiments

Anion Ion Exchange Chromatography: Stick/Strip Via Screening Electrostatics



Initially (2003) Separation Only Between Semiconductor And Metallic Classes

- M. Zheng And Et. Al., **Science,** 302, 1545 (2003)



Years Later (2006), Separate Semiconductors Of Identical Diameter/Band Gap

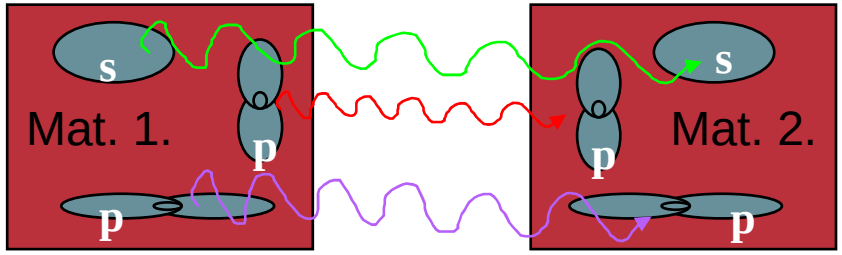
- M. Zheng And E. D. Semke, **J. Am. Chem. Soc.,** 129, 6084 (2007)

Question: Do Known SWCNT Band Gap Trends Also Contribute A Chirality Dependent Vdw-ld Interaction To Assist This Process?

Origin of The vdW-London Dispersion Interaction

London Dispersion Interactions

- Of the Van der Waals Interaction
- Thermodynamic Free Energy



Arises From Oscillating Dipoles

- Interatomic Bonds of Electronic Structure

J_{cv} => London Disp. Spectra

A - Hamaker Constant

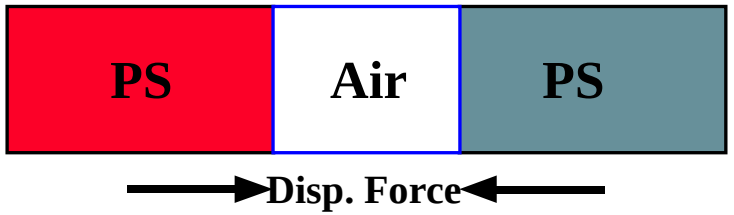
- Interaction Scaling Constant

$$E_{vdW-Ld} = -\frac{A(l)}{12\pi l^2}$$

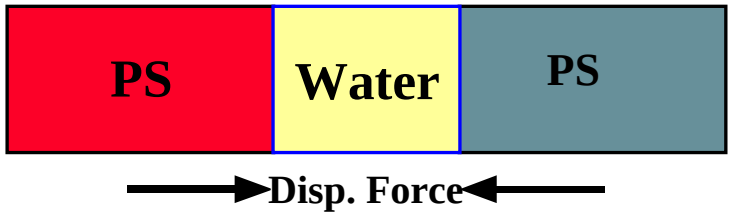
F_{vdW-Ld} - Dispersion Force

Attractive Force: Nonwetting

- **Positive Hamaker Constant**



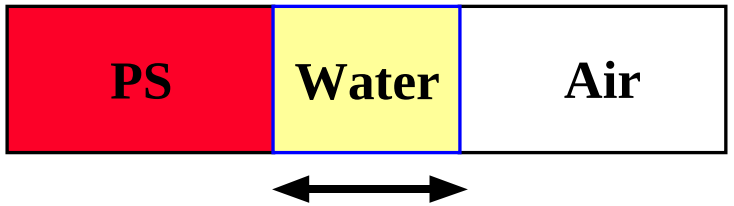
A_{123} 71 zJ



8 zJ

Repulsive Force: Wetting

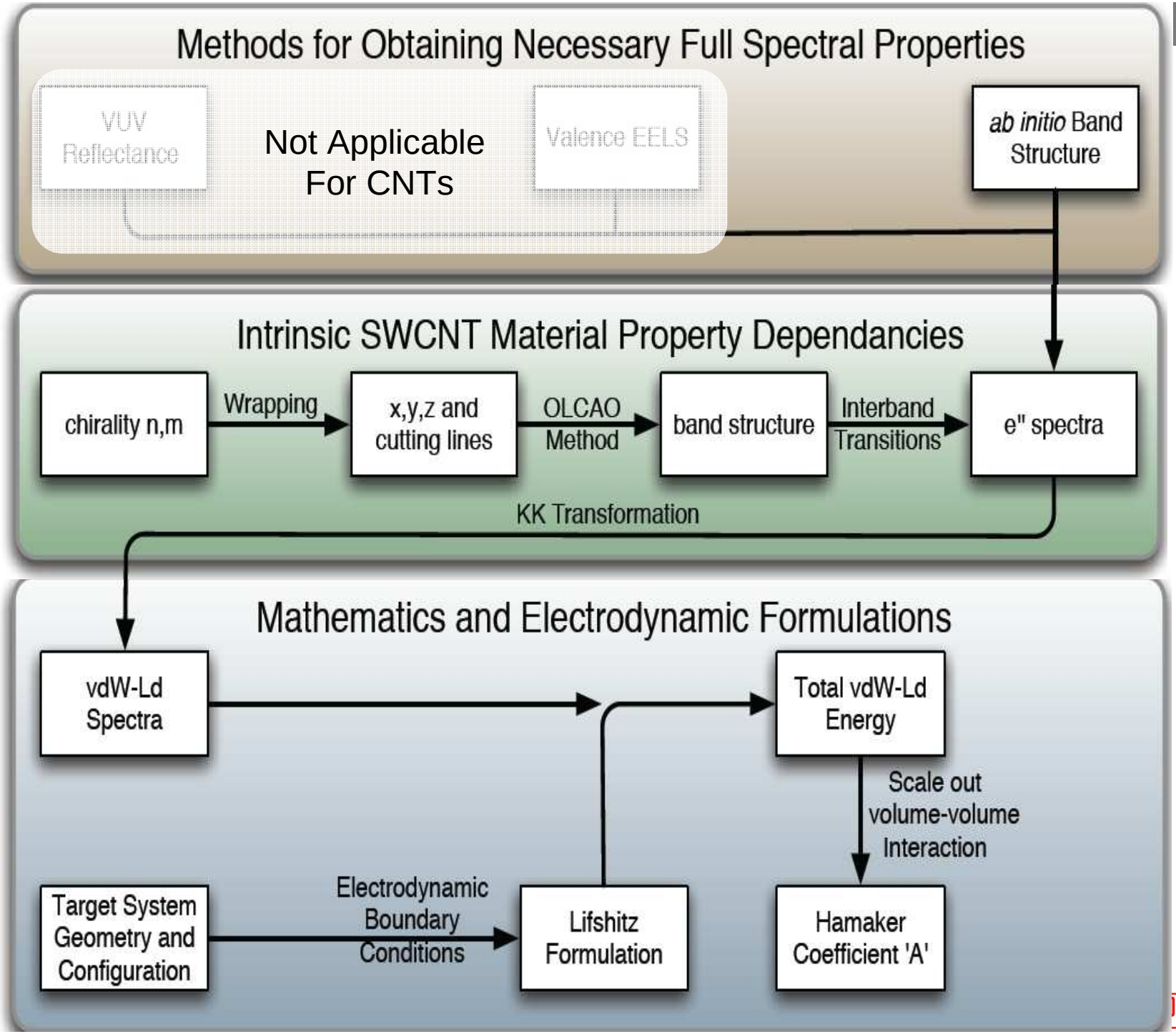
- **Negative Hamaker Constant**



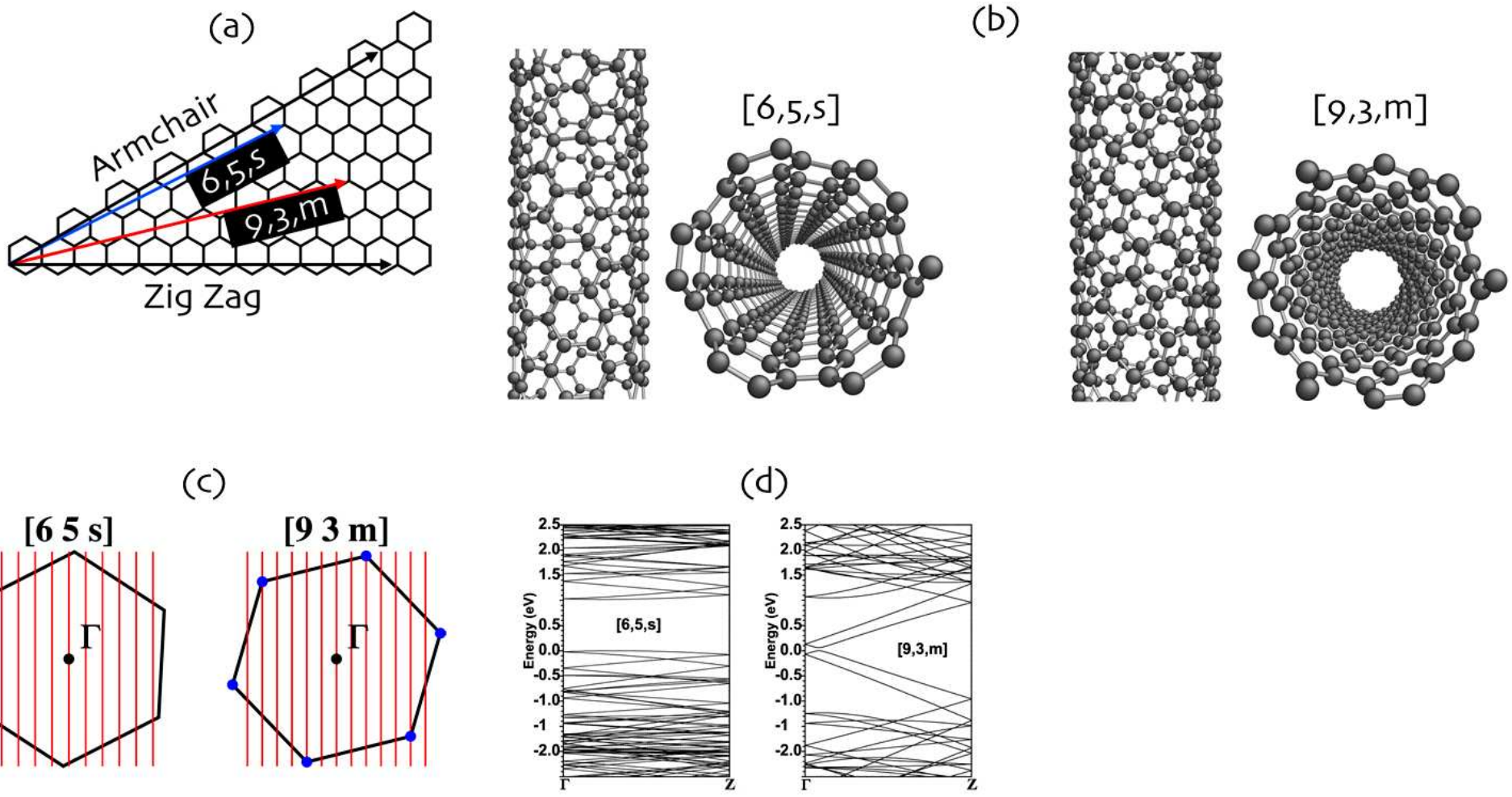
-16 zJ

zJ = zeptoJoule = 10^{-21} Joules

R. H. French, **J. Amer. Ceram. Soc., 83,** 9, 2117-46 (2000).
R. H. French, K. I. Winey, M. K. Yang, W. Qiu, **Aust. J. Chem., 60**, 251-63, (2007).

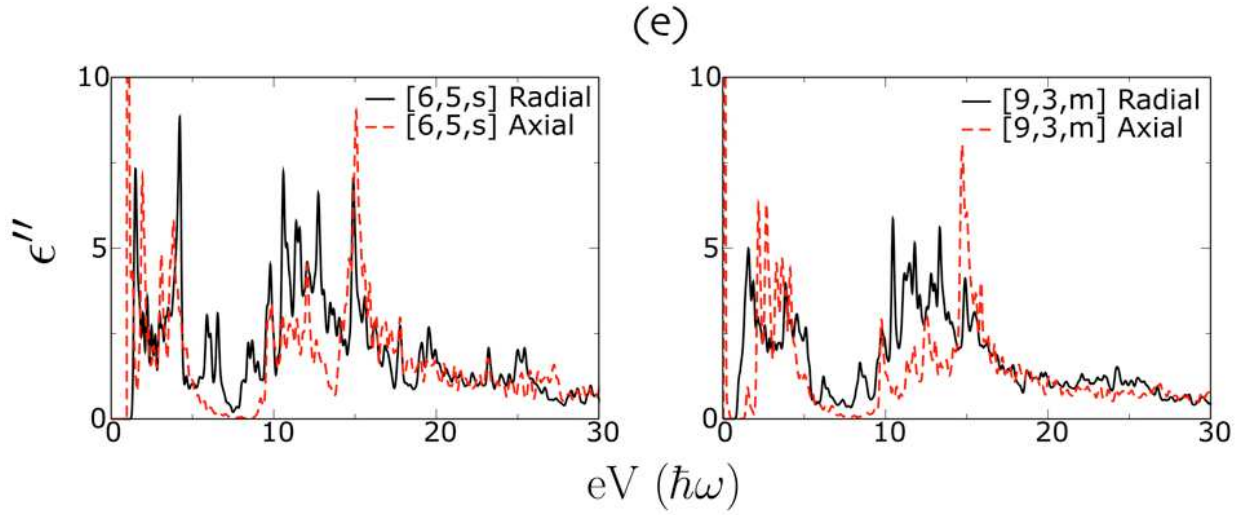

Methods for Obtaining Necessary Full Spectral Properties
VUV Reflectance
Not Applicable For CNTs
Valence EELS
ab initio Band Structure
Intrinsic SWCNT Material Property Dependancies
chirality n,m
Wrapping
x,y,z and cutting lines
OLCAO Method
band structure
Interband Transitions
e" spectra
KK Transformation
Mathematics and Electrodynamic Formulations
vdW-Ld Spectra
Total vdW-Ld Energy
Scale out volume-volume Interaction
Target System Geometry and Configuration
Electrodynamic Boundary Conditions
Lifshitz Formulation
Hamaker Coefficient 'A'

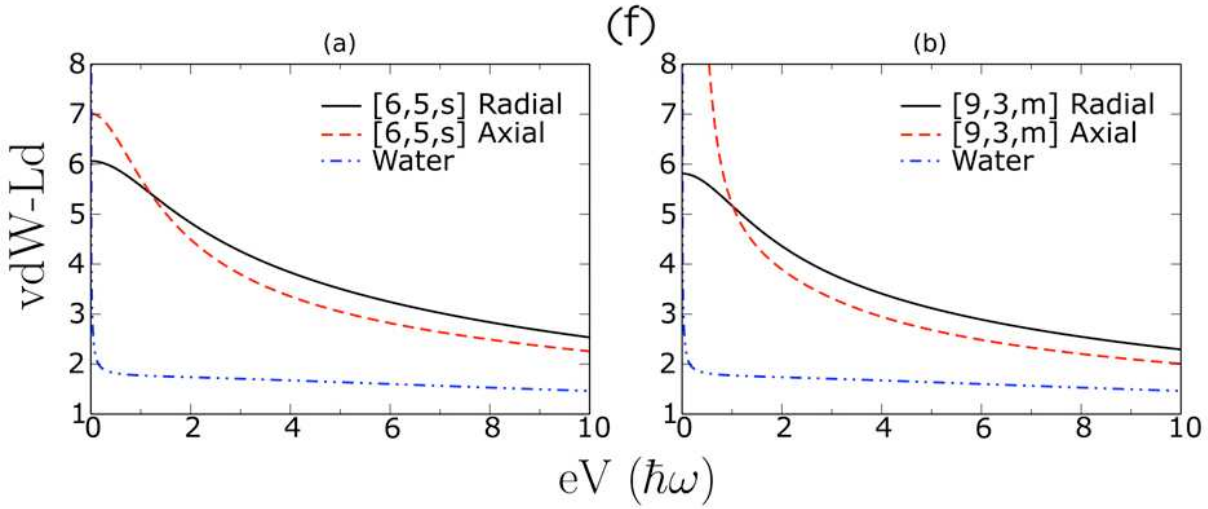
SWCNTs: All Layers of Abstraction Part A

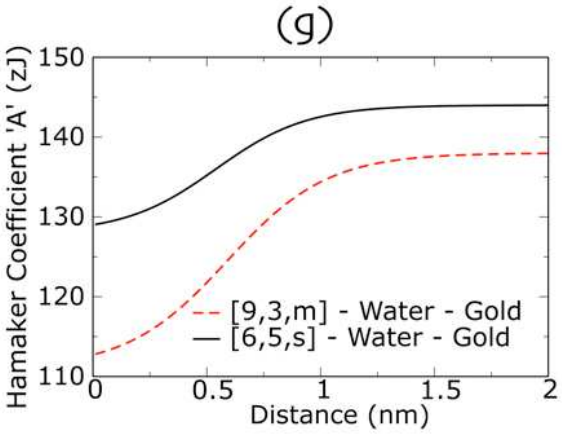


P. Lambin, **C. R. Phys**. 4, 1009 2003.

SWCNTs: All Layers of Abstraction Part B







$$\epsilon(i\xi) = 1 + \frac{2}{\pi}\int_0^\infty \frac{\epsilon''(\omega)d\omega}{\omega^2+\xi^2}$$

Ab initio Optical Properties Of Graphene And SWCNTs

Density Functional, OLCAO Calculations

Of

Electronic Structure and Optical Properties

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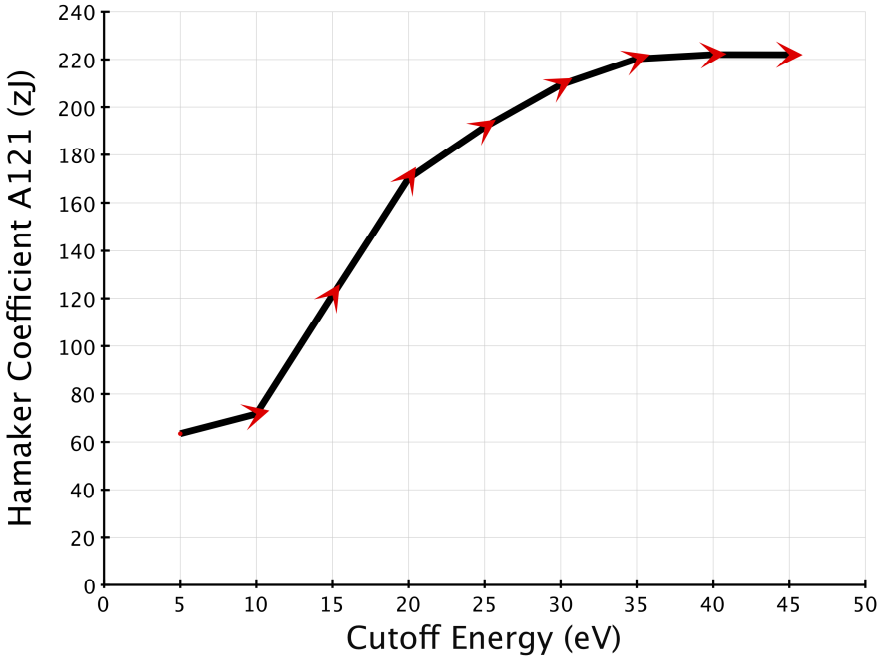
Optical Properties 1: Introducing ab-initio Method

Needs ε'' Spectra From 0 To 30+ eV

Many CNT Studies Use Tight Binding Approximation

- Forces An Unrealistic Symmetry Of Conduction/Valence Bands
- Distorts Optical Properties
- Typically 0-6 eV



ab initio Electronic Structure Calculation

- Basis Set Up To 3d And 4s
- ALL Single Electron Transitions From 0 To 45+ eV
- Robust: Al2o3 ab initio And Experimental Results Are Comparable To ~ 30 eV
  - W. Y. Ching And et. al., J. Phys. Condensed Matter 16, 2891 (2004)

$$\epsilon''_{ij}(\omega) = \frac{4\pi^2 e^2}{\Omega m^2 \omega^2} \sum_{knn'\sigma} \langle kn\sigma|p_i|kn'\sigma\rangle\langle kn'\sigma|p_j|kn\sigma\rangle f_{kn}(1-f_{kn'})\delta(e_{kn'}-e_{kn}-\hbar\omega).$$

Graphene: Partial Density Of States

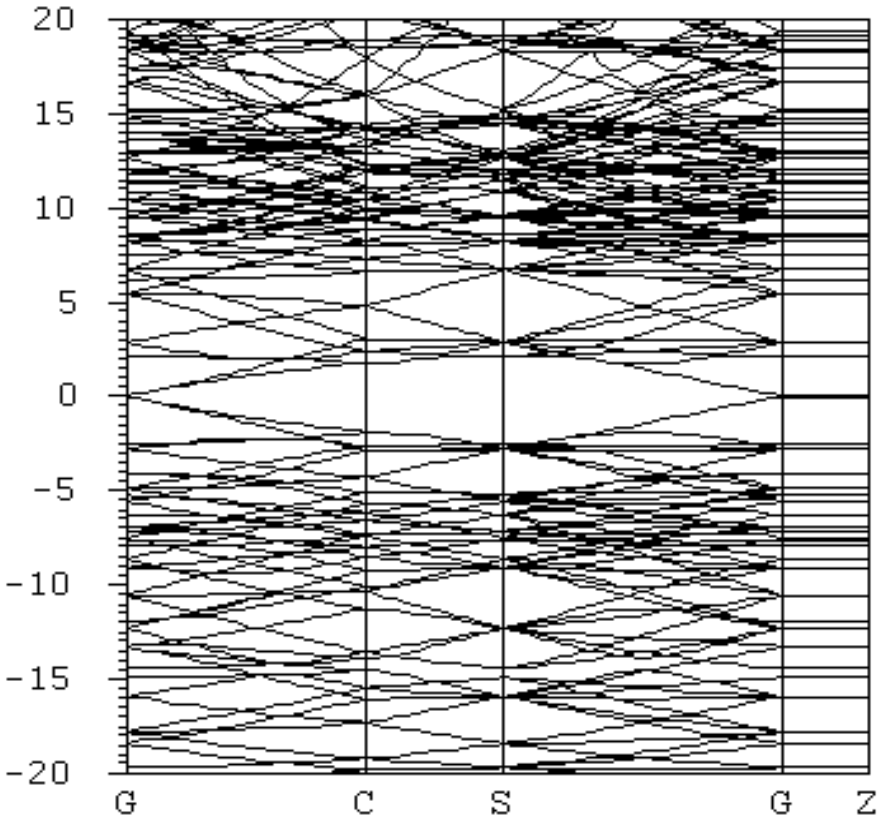
π Bond Arise From Out-Of-Plane p_z Orbitals

- πUpper Valence & Lower Conduction Bands

Transport Properties Of CNTs From π Bonds

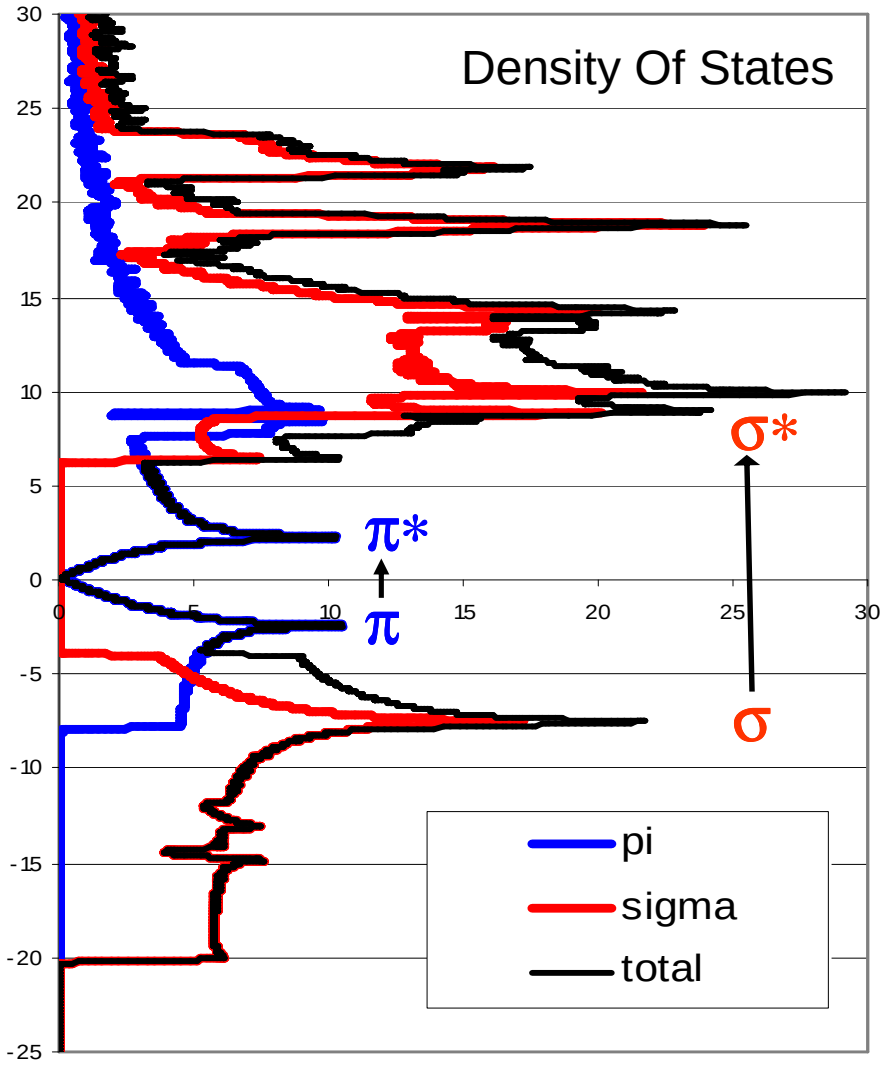
- "Band" Metals vs. "Optical" Metals (Drude Metal Peak)

Optical Properties From π & σ Bonds



π Bond: From p_z

σ Bond: From Sp^2 Hybridization s, p_x, p_y



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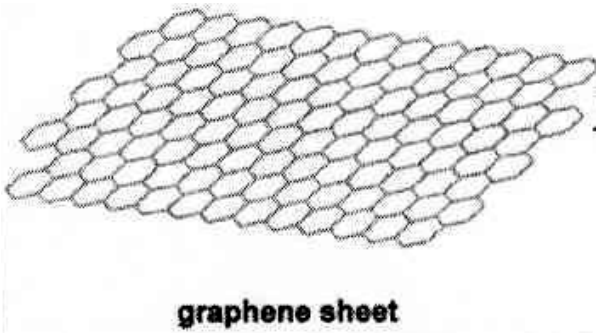
Graphene: Ab initio Optical Properties



Graphene: A Semi-metal

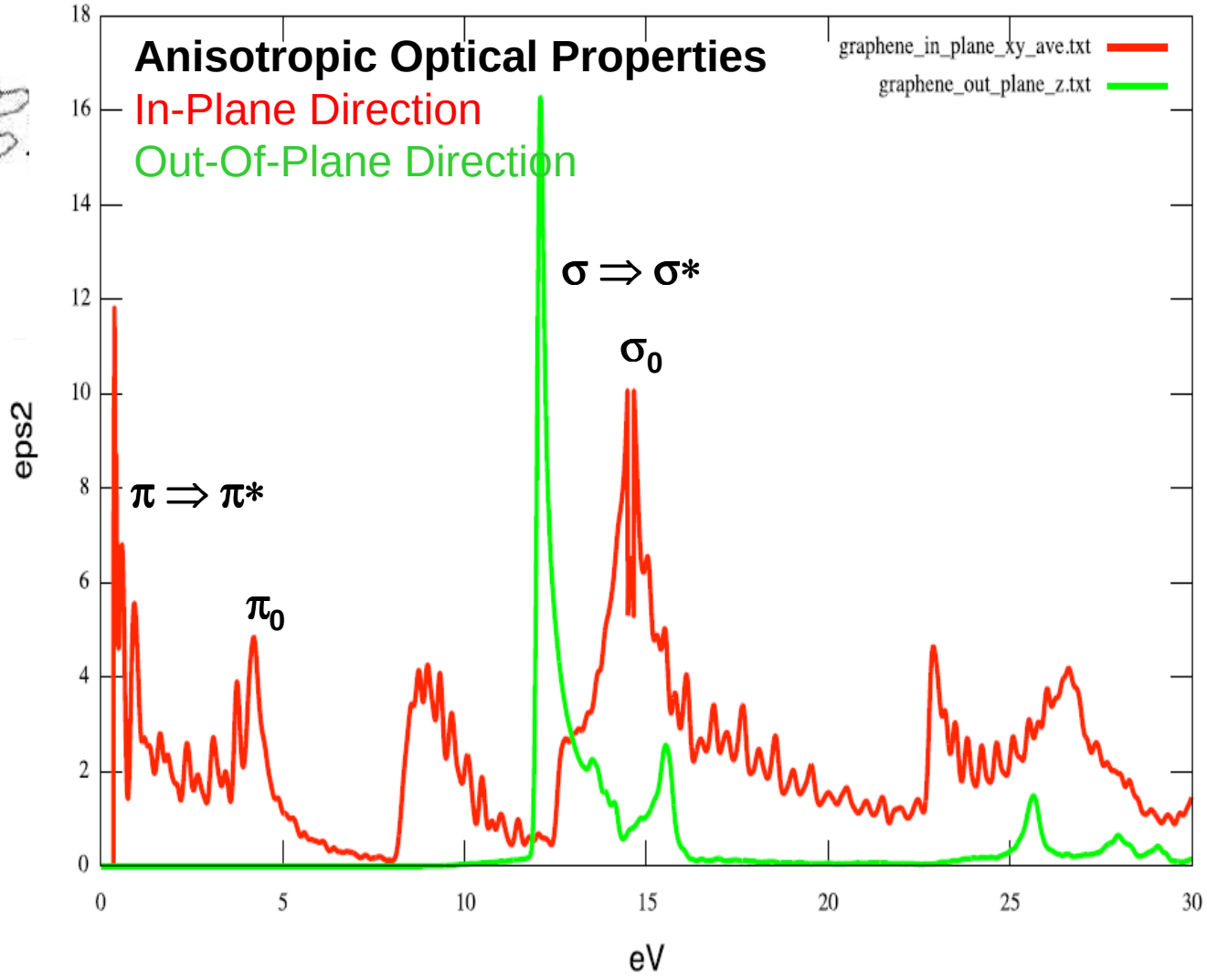
- In Plane

Low DOS At Gap

- No 0 eV Drude Metal Peak

Higher Energy Transitions

- From σ (s, p_x, p_y) Bonds
- sp_2 Hyrbridization



60 SWCNTs

OLCAO Band Structure Calculations

- Density Functional Theory

Armchair "Metals"

Zigzag Metal

Zigzag Semi

Chiral Metal

Chiral Semi

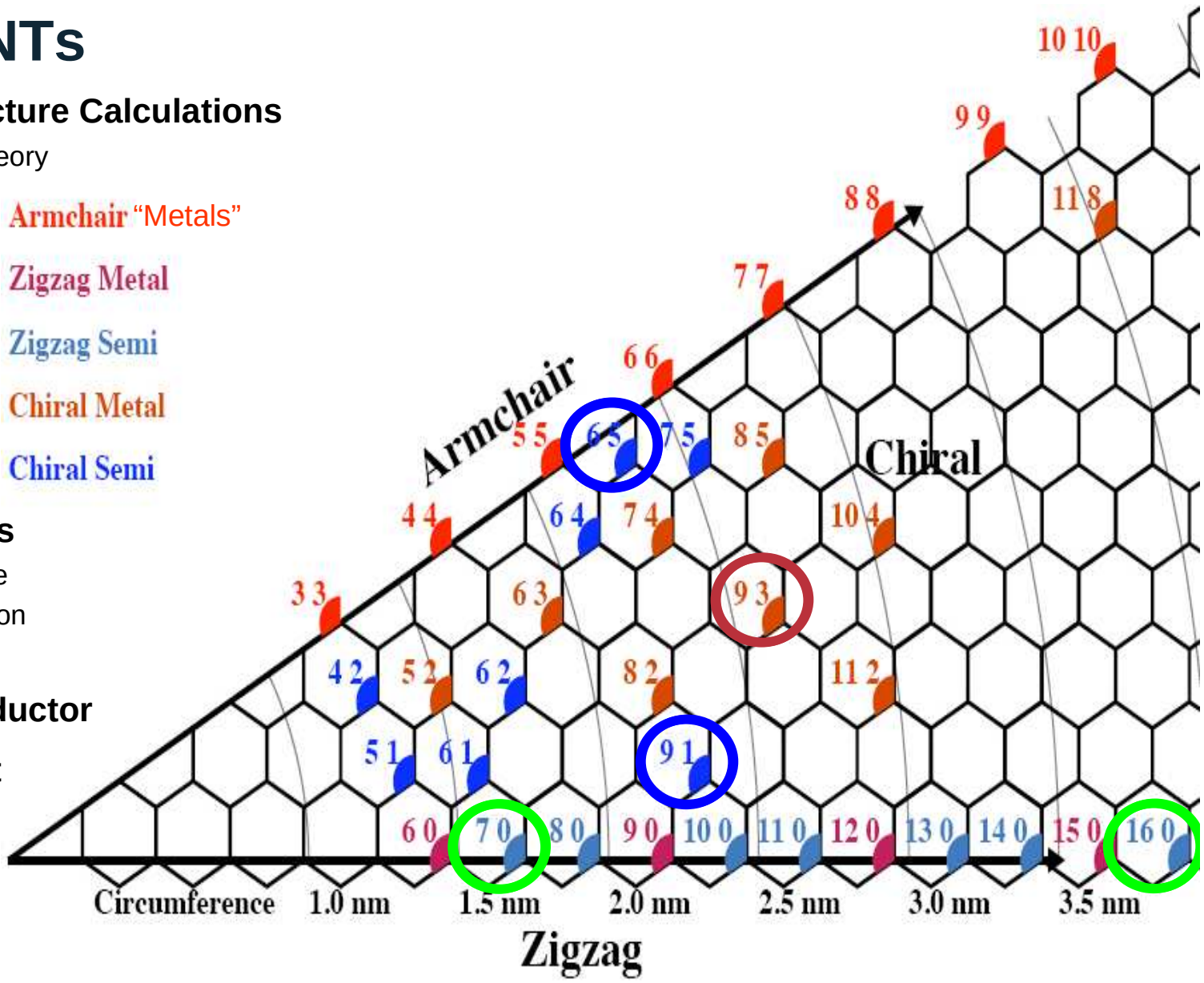
Atomic Coordinates

- From Rolled Graphene
- No Structural Relaxation

Metal vs. Semiconductor

Elution Experiment

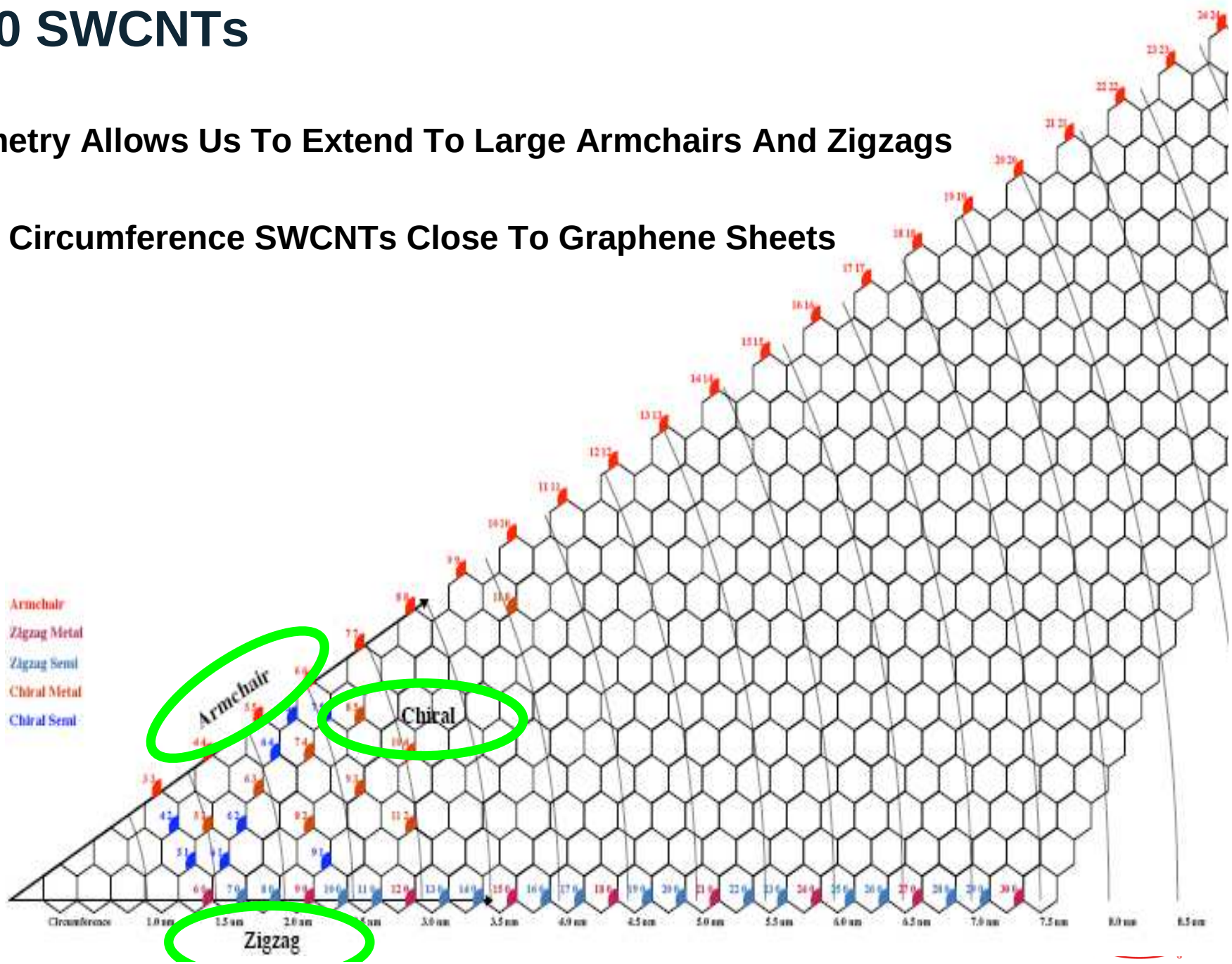
Multi-wall CNTs



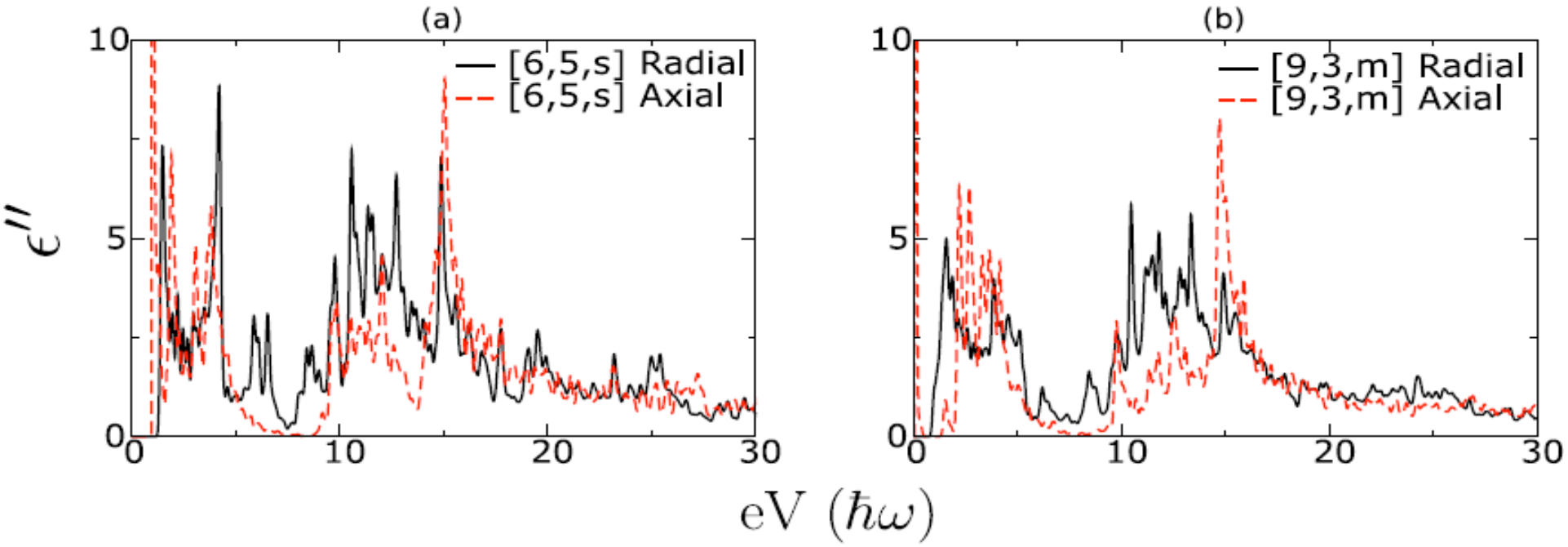
60 SWCNTs

Symmetry Allows Us To Extend To Large Armchairs And Zigzags

Large Circumference SWCNTs Close To Graphene Sheets



[6,5,s] & [9,3,m] SWCNT: Uniaxial Optical Properties

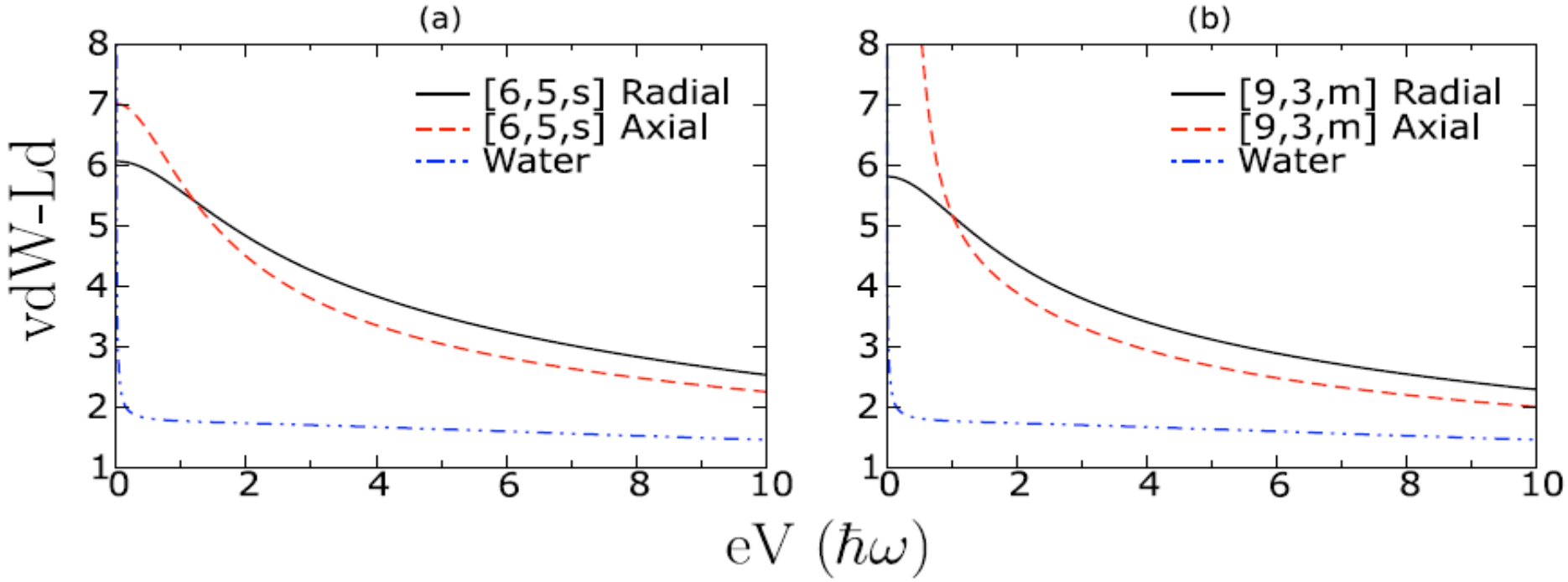


Radial Directions Have Similar Properties

Axial Directions Very Different

- Due To Metallic Axial Property Of [9,3,m]
  - [9,3,m] ε" Max of 933 at 0.04 eV

$\varepsilon''(i\xi)$ London Disp. Spectra Of [6,5,s] & [9,3,m] CNTs



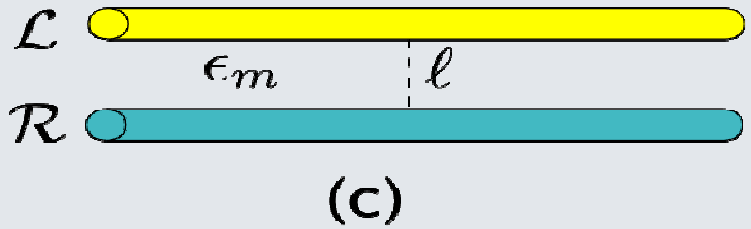
LDS Crossings => Complex Behavior

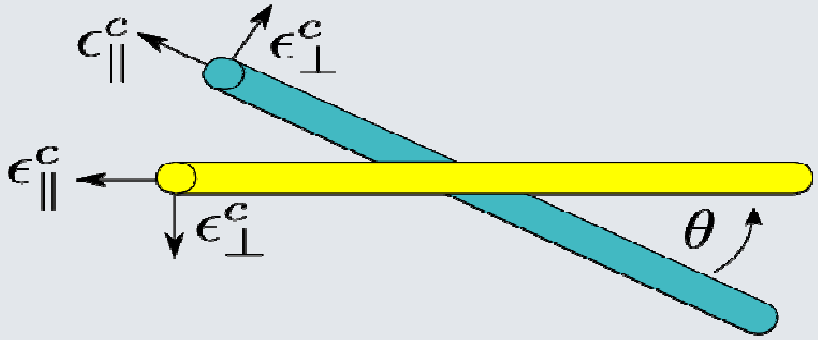
- e.g. Surficial Films Of Water On Ice

Water vdW-Ld Spectrum Max of 78 at 0 eV

[9,3,m] vdW-Ld Spectrum Max of 333 at 0 eV

Optically And Morphologically Anisotropic Solid Cylinders





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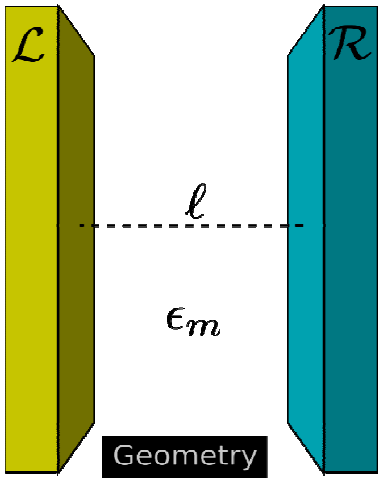
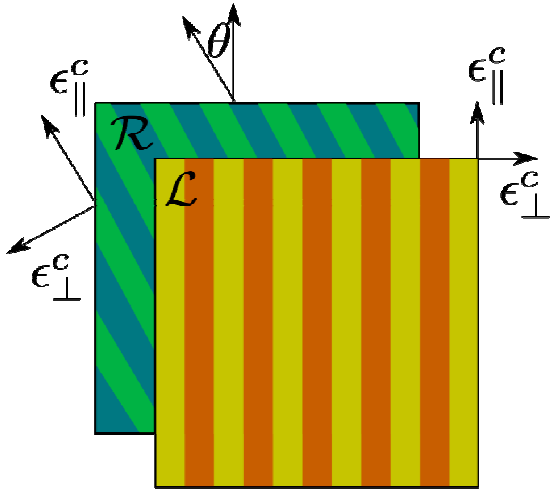
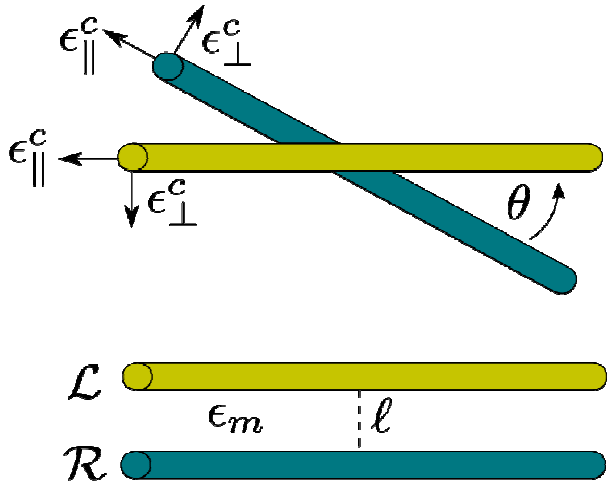
R. Rajter, R. Podgornik, V. A Parsegian, R. H. French, W. Y. Ching, **Physical Review B., 76**, 045417 (2007).

Formulation: Derivation & Comparison to Simple Systems

70+ Equation Derivation. Here's The Punch Line

(a)	(b)	(c)
		
Geometry		
$G(\ell) = -\frac{\mathcal{A}}{12\pi\ell^2}$	$G(\ell,\theta) = -\frac{\mathcal{A}^{(0)}+\mathcal{A}^{(2)}\cos^2\theta}{12\pi\ell^2}$	$G(\ell,\theta) = -\frac{(\pi a^2)^2(\mathcal{A}^{(0)}+\mathcal{A}^{(2)}\cos^2\theta)}{2\pi\ell^4\sin\theta}$ $G(\ell,\theta=0) = -\frac{3(\pi a^2)^2(\mathcal{A}^{(0)}+\mathcal{A}^{(2)})}{8\pi\ell^5}$
Energy		
$\mathcal{A} = \frac{3}{2}k_BT{\sum_{n=0}^{\infty}}' \Delta_{\mathcal{L}m}\Delta_{\mathcal{R}m}$	$\mathcal{A}^{(0)} = \frac{3}{2}k_BT{\sum_{n=0}^{\infty}}' \frac{1}{2\pi}\int_0^{2\pi}\Delta_{\mathcal{L}m}(\phi)\Delta_{\mathcal{R}m}(\phi-90)d\phi$ $\mathcal{A}^{(0)}+\mathcal{A}^{(2)} = \frac{3}{2}k_BT{\sum_{n=0}^{\infty}}' \frac{1}{2\pi}\int_0^{2\pi}\Delta_{\mathcal{L}m}(\phi)\Delta_{\mathcal{R}m}(\phi)d\phi$	$\mathcal{A}^{(0)} = \frac{3}{2}k_BT{\sum_{n=0}^{\infty}}' \frac{1}{2\pi}\int_0^{2\pi}\Delta_{\mathcal{L}m}(\phi)\Delta_{\mathcal{R}m}(\phi-90)d\phi$ $\mathcal{A}^{(0)}+\mathcal{A}^{(2)} = \frac{3}{2}k_BT{\sum_{n=0}^{\infty}}' \frac{1}{2\pi}\int_0^{2\pi}\Delta_{\mathcal{L}m}(\phi)\Delta_{\mathcal{R}m}(\phi)d\phi$
Hamaker Coefficients		
$\Delta_{\mathcal{L}m} = \left(\frac{\epsilon_{\mathcal{L}}-\epsilon_m}{\epsilon_{\mathcal{L}}+\epsilon_m}\right)$ $\Delta_{\mathcal{R}m} = \left(\frac{\epsilon_{\mathcal{R}}-\epsilon_m}{\epsilon_{\mathcal{R}}+\epsilon_m}\right)$	$\Delta_{\mathcal{L}m}(\phi) = \left(\frac{\epsilon_\perp(\mathcal{L})\sqrt{1+\gamma(\mathcal{L})\cos^2\phi}-\epsilon_m}{\epsilon_\perp(\mathcal{L})\sqrt{1+\gamma(\mathcal{L})\cos^2\phi}+\epsilon_m}\right)$ $\Delta_{\mathcal{R}m}(\phi) = \left(\frac{\epsilon_\perp(\mathcal{R})\sqrt{1+\gamma(\mathcal{R})\cos^2\phi}-\epsilon_m}{\epsilon_\perp(\mathcal{R})\sqrt{1+\gamma(\mathcal{R})\cos^2\phi}+\epsilon_m}\right)$ $\Delta_{\mathcal{R}m}(\phi-90) = \left(\frac{\epsilon_\perp(\mathcal{R})\sqrt{1+\gamma(\mathcal{R})\sin^2\phi}-\epsilon_m}{\epsilon_\perp(\mathcal{R})\sqrt{1+\gamma(\mathcal{R})\sin^2\phi}+\epsilon_m}\right)$	$\Delta_{\mathcal{L}m}(\phi) = -\left(\Delta_\perp(\mathcal{L}) + \frac{1}{4}(\Delta_\parallel(\mathcal{L}) - 2\Delta_\perp(\mathcal{L}))\cos^2\phi\right)$ $\Delta_{\mathcal{R}m}(\phi) = -\left(\Delta_\perp(\mathcal{R}) + \frac{1}{4}(\Delta_\parallel(\mathcal{R}) - 2\Delta_\perp(\mathcal{R}))\cos^2\phi\right)$ $\Delta_{\mathcal{R}m}(\phi-90) = -\left(\Delta_\perp(\mathcal{R}) + \frac{1}{4}(\Delta_\parallel(\mathcal{R}) - 2\Delta_\perp(\mathcal{R}))\sin^2\phi\right)$
Spectra Functions		
Anisotropy Pieces	$\gamma = \frac{\epsilon_\parallel-\epsilon_\perp}{\epsilon_\perp}$	$\Delta_\parallel = \frac{\epsilon_\parallel-\epsilon_m}{\epsilon_m}$ $\quad$ $\Delta_\perp = \frac{\epsilon_\perp-\epsilon_m}{\epsilon_\perp+\epsilon_m}$

R. F. Rajter, R. Podgornik, V. A. Parsegian, R. H. French, W. Y. Ching, **Phys. Rev. B** 76, 045417 (2007).

R. F. Rajter and R. H. French, J**. Phys.: Conf. Ser**. 94, 012001, (2008).

The Devil's in the Delta's

All Systems Have Identical Summations

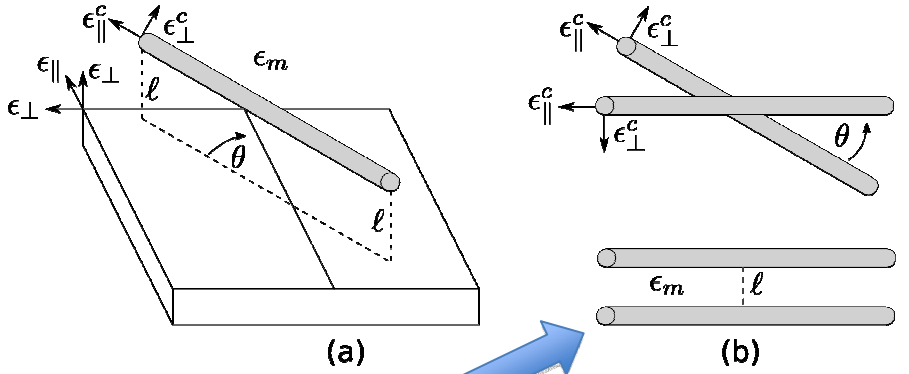
$$\mathcal{A} = \frac{3kT}{2} * \frac{1}{2\pi} \int_{\phi=0}^{2\pi} \sum_{n=0,1,2..}^{\infty}{}' \Delta_{ij} * \Delta_{kj}\, d\phi \qquad \Delta_{ij} = \frac{\epsilon_i - \epsilon_j}{\epsilon_i + \epsilon_j} \qquad \Delta_{kj} = \frac{\epsilon_k - \epsilon_j}{\epsilon_k + \epsilon_j}$$

Changing Δ's Changes How The Optical Contrast Is Weighted

$$\Delta_{\mathcal{L}m}(\phi) = \left(\frac{\epsilon_\perp(\mathcal{L})\sqrt{1+\gamma(\mathcal{L})\cos^2\phi} - \epsilon_m}{\epsilon_\perp(\mathcal{L})\sqrt{1+\gamma(\mathcal{L})\cos^2\phi} + \epsilon_m} \right)$$

$$\Delta_{\mathcal{R}m}(\phi) = \left(\frac{\epsilon_\perp(\mathcal{R})\sqrt{1+\gamma(\mathcal{R})\cos^2(\phi-\theta)} - \epsilon_m}{\epsilon_\perp(\mathcal{R})\sqrt{1+\gamma(\mathcal{R})\cos^2(\phi-\theta)} + \epsilon_m} \right)$$

$$\gamma = \frac{\epsilon_\parallel - \epsilon_\perp}{\epsilon_\perp}$$



$$\Delta_{\mathcal{L}m}(\phi) = -\left(\Delta_\perp(\mathcal{L}) + \tfrac{1}{4}(\Delta_\parallel(\mathcal{L}) - 2\Delta_\perp(\mathcal{L}))\cos^2\phi\right)$$

$$\Delta_{\mathcal{R}m}(\phi) = -\left(\Delta_\perp(\mathcal{R}) + \tfrac{1}{4}(\Delta_\parallel(\mathcal{R}) - 2\Delta_\perp(\mathcal{R}))\cos^2(\phi-\theta)\right)$$

$$\Delta_\parallel = \frac{\epsilon_\parallel - \epsilon_m}{\epsilon_m} \qquad \Delta_\perp = \frac{\epsilon_\perp - \epsilon_m}{\epsilon_\perp + \epsilon_m}$$

Hamaker Coefficient Dependencies

- Material Properties (Optical Inputs)
- Geometry (Changes Spectral Mismatch / Weighting Functions)

R. F. Rajter, R. Podgornik, V. A. Parsegian, R. H. French, W. Y. Ching, **Phys. Rev. B** 76, 045417 (2007).

Separation (S2SS) And Angle Dependence

Equally Important: Surface-To-Surface Separation Scaling

$$g(\ell,\theta,a) = -\frac{\sqrt{2a}\ \left(\mathcal{A}^{(0)} + \mathcal{A}^{(2)}\cos^2\theta\right)}{24\ \ell^{3/2}}.$$

Rod-Substrate Near-Limit

$$g(\ell,\theta) = -\frac{(\pi a^2)\ \left(\mathcal{A}^{(0)} + \mathcal{A}^{(2)}\cos^2\theta\right)}{6\pi\ \ell^3}$$

Rod-Substrate Far-Limit

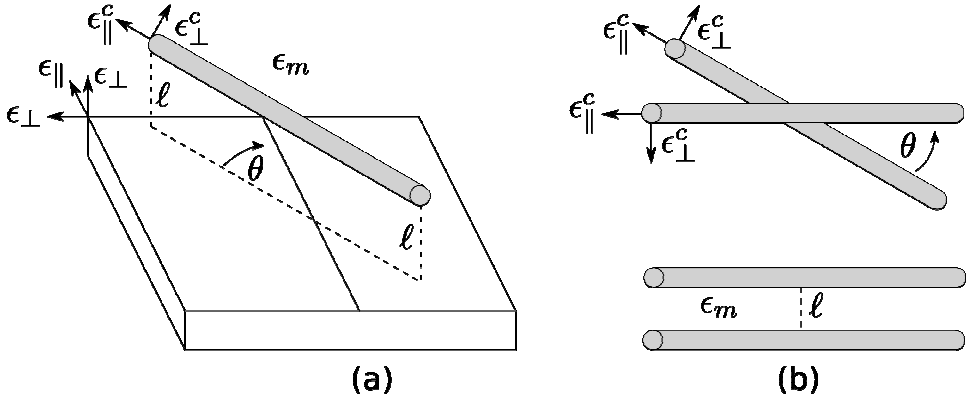
Optical Anisotropy Determines Angle-dependent Interactions Of Rod-Substrate

$$G(\ell,\theta;a) = -\frac{a}{6\ \ell\ \sin\theta}\left(\mathcal{A}^{(0)} + \mathcal{A}^{(2)}\cos^2\theta\right)$$

Rod-Rod Near-Limit

$$G(\ell,\theta) = -\frac{(\pi a^2)^2\left(\mathcal{A}^{(0)} + \mathcal{A}^{(2)}\cos^2\theta\right)}{2\pi\ \ell^4\ \sin\theta}.$$

Rod-Rod Far-Limit



Optical Anisotropy & Shape Affect Angle-dependent Interactions For Rod-Rod

R. F. Rajter, R. Podgornik, V. A. Parsegian, R. H. French, W. Y. Ching, **Phys. Rev. B** 76, 045417 (2007).

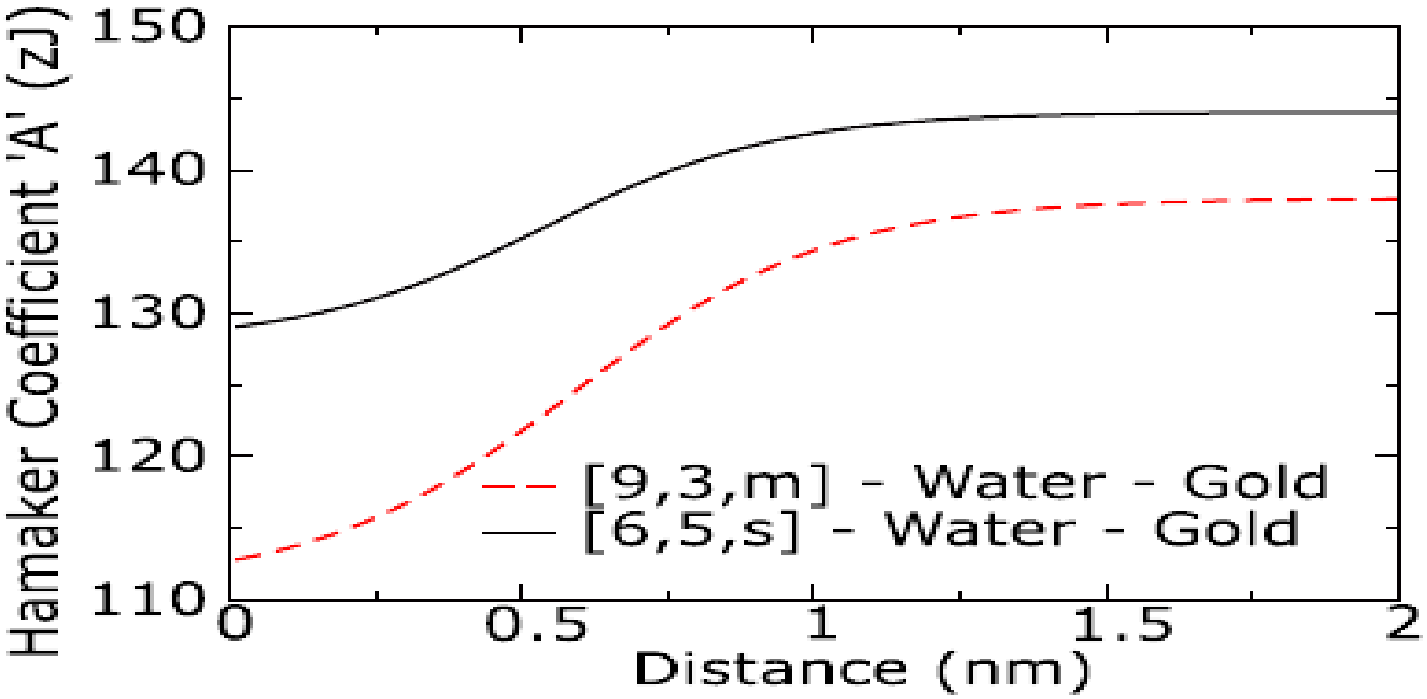
Hamaker Coefficients Versus distance

Near Limit

$$\gamma = \frac{\epsilon_{\parallel} - \epsilon_{\perp}}{\epsilon_{\perp}}$$

Far Limit

$$\Delta_{\parallel} = \frac{\epsilon_{\parallel} - \epsilon_{m}}{\epsilon_{m}}$$



Near Limit Is < 2 Diameters, And Far Limit Is > 2 Diameters

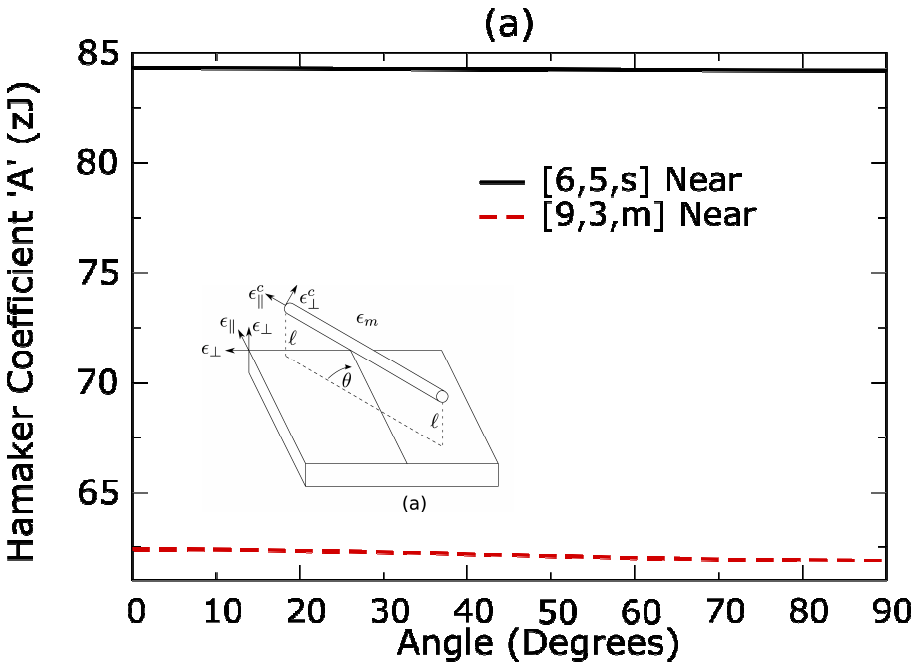
Semiconducting CNT's Hamaker Coefficient Larger Than Metallic

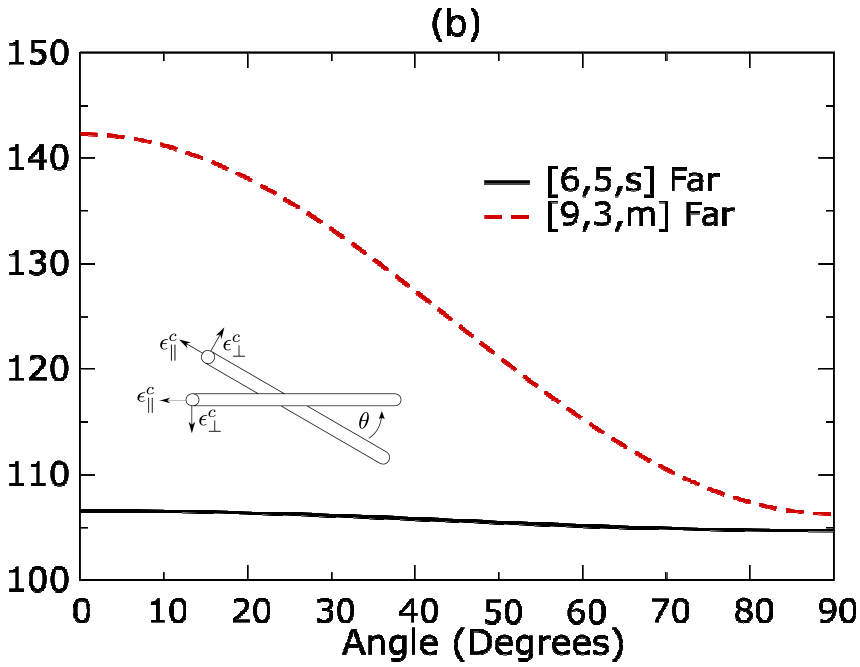
Far Limit Hamaker Coeff.s Larger Than Near Limit

- Due To Δ parallel

Alignment Forces of Interacting Rods

vdW-Ld Torques Arise When There Is A Preferred Interaction Direction





$$g(\ell,\theta,a) = -\frac{\sqrt{2a}\ \left(\mathcal{A}^{(0)} + \mathcal{A}^{(2)}\cos^2\theta\right)}{24\ \ell^{3/2}}.$$

Rod-Substrate Near-Limit

$$G(\ell,\theta) = -\frac{(\pi a^2)^2\left(\mathcal{A}^{(0)} + \mathcal{A}^{(2)}\cos^2\theta\right)}{2\pi\ \ell^4\ \sin\theta}.$$

Rod-Rod Far-Limit

Again, Any Rod-substrate Alignment Is Purely Due To Optical Properties

Rod-rod Alignment Can Have Optical And Geometrical Effects

vdW-Ld Interactions Of SWCNTs

vdW-Ld Interactions In The Elution Experiment

Mixing: Hollow Cylinders And Large Diameter CNTs

Multi-wall Carbon Nanotubes

Datamining 60 CNTs: Trends And Classification

DUPONT®

The miracles of science™

We Can Now Answer Elution Question: Optical Properties & vdW-Ld Vary With Chirality

Separation Is Repeatable And Distinct

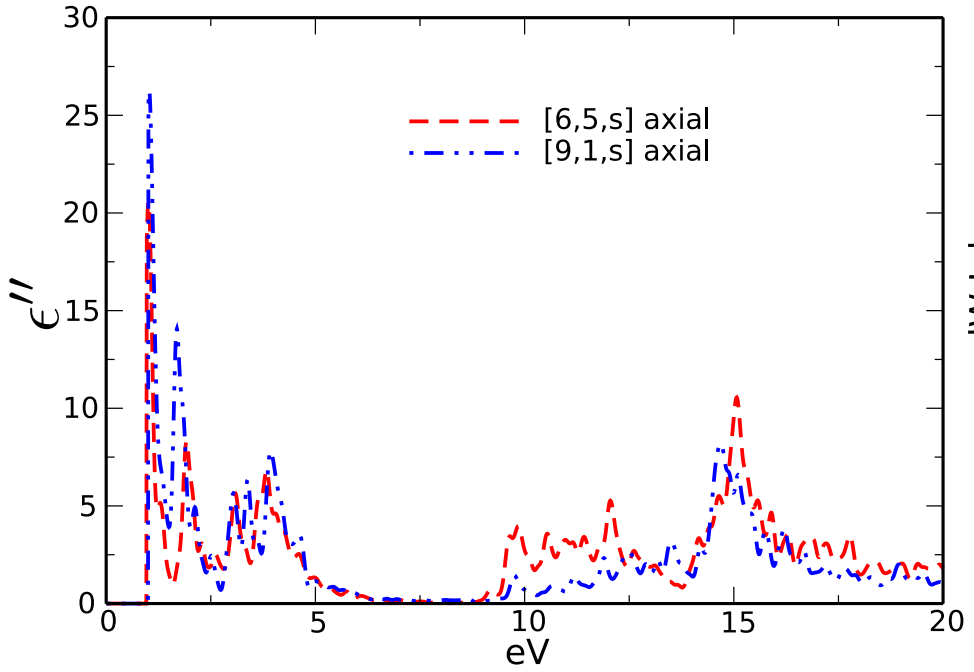
Even Between SWCNTs Of Identical Band Gap And Radius

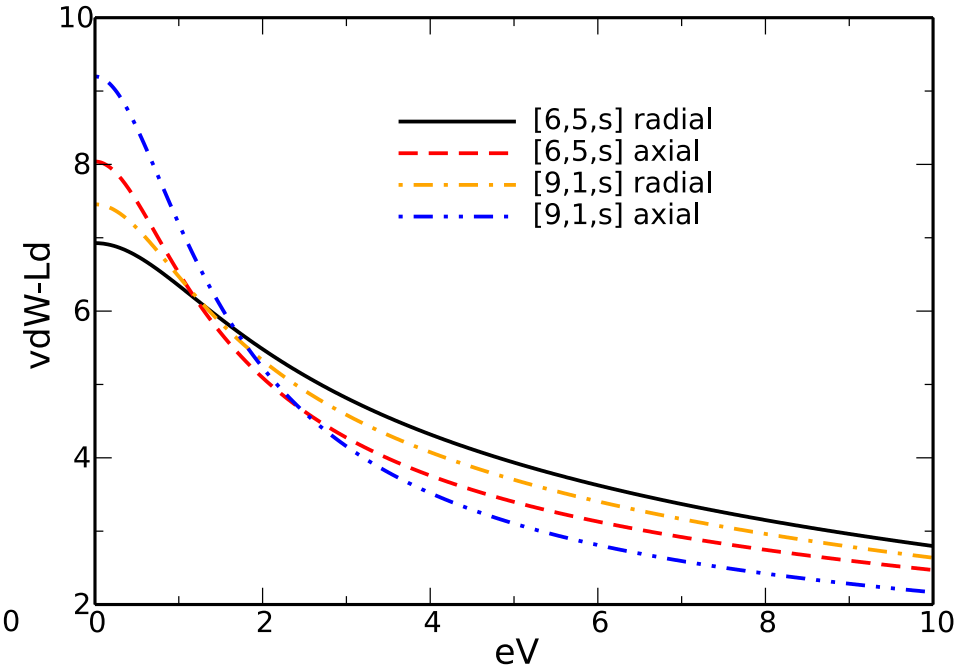
- e.g. [6,5,s] Versus [9,1,s])

Analysis Of The Optical Properties Shows There Is A Difference

The Overall Theme

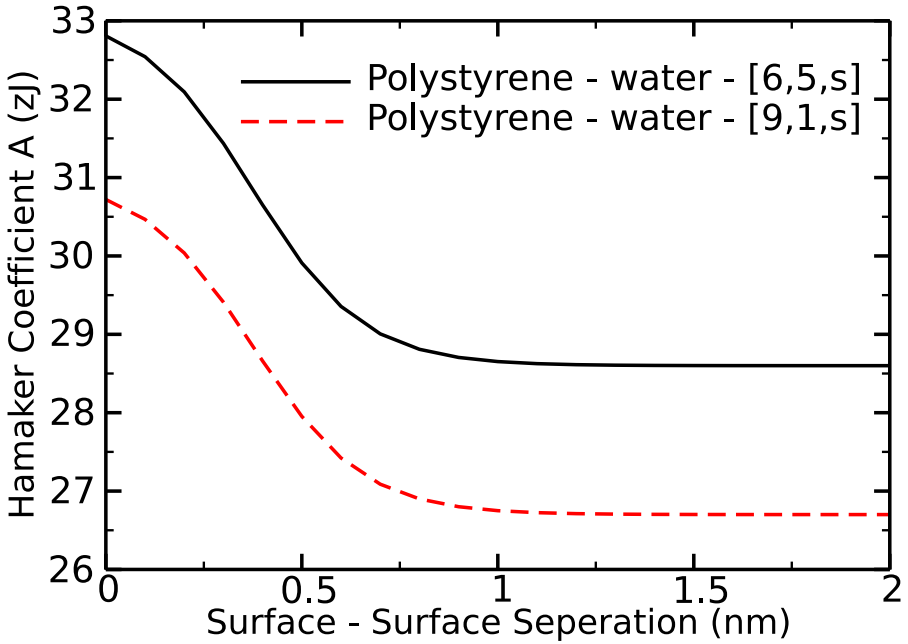
- Chirality => Geometry => Band Structure => Optical Properties => vdW-Ld Interactions





Consider Axial Directions

Elution Experiment Example Summary



There Is A 5% Difference In The Hamaker Coefficients For [6,5,s] And [9,1,s]

- This Correlates With The Experimentally Observed Trend

Even Though These Tubes Are Almost Identical

- Their Dispersion Interaction Distinguishes Them

Demonstrates The Utility Of Full Spectra Optical Properties Of Materials

Now Consider Other Materials To Enhance Or Mitigate Elution

- By Calculating the Hamaker Coefficients Of A (Substrate | Medium | SWCNT)

Mixing: Hollow Cylinders And Large Diameter CNTs

Multi-wall Carbon Nanotubes

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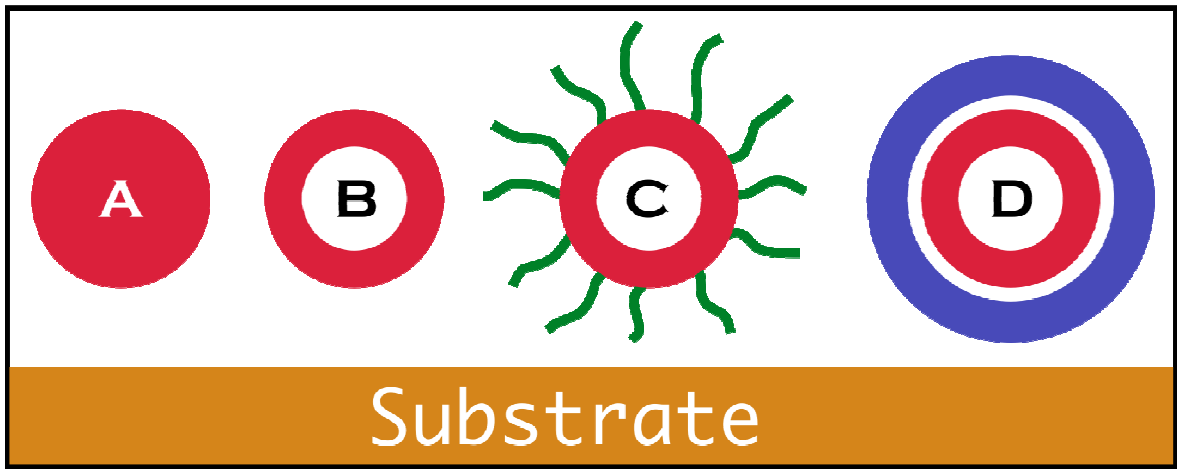
The miracles of science™

Real SWCNTs Versus Solid Cylinders

Real SWCNTs Are Hollow And Have Surfactants

- Large Diameter CNTs Could Be Filled



Current "Solid Cylinder" Formulations Have No Means For Such An Input

- No Add-a-layer Like Solution Exists (e.g. Plane-plane Geometry)

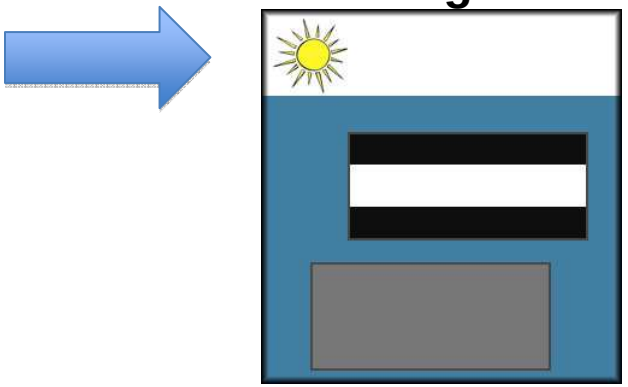
However, Can Create Effective "Bulk Averaged" Spectra By Optical Mixing

- Typically Done For Optical Properties Of Composites (e.g. Metal In Glass)
- Using Bruggeman Effective Medium Approximation

Blending the Components Into One Material

Multi-component Materials Can Be Blended Into Bulk Average

- Use Effective Medium Approximation

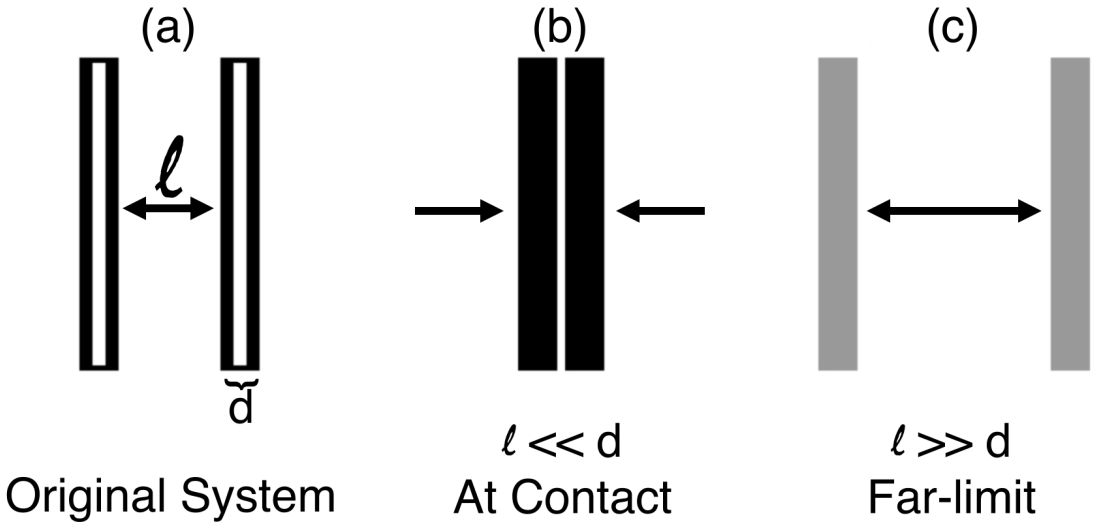


One Key Detail Remains…

- **What To Use In Near Limit, At Contact?**
- **What To Use At Far Limit?**

A Typical Rule Of Thumb Is Thus:

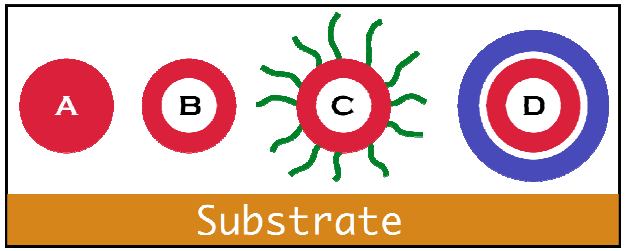
- If S2ss > 2 * Feature Size, Mixing Can Be Used
- If Close To Contact, No Mixing Because Outer Material Interactions Dominate
- In Far Limit Use Mixing Result For Optical Properties



EMA + Parallel Capacitor Mixing

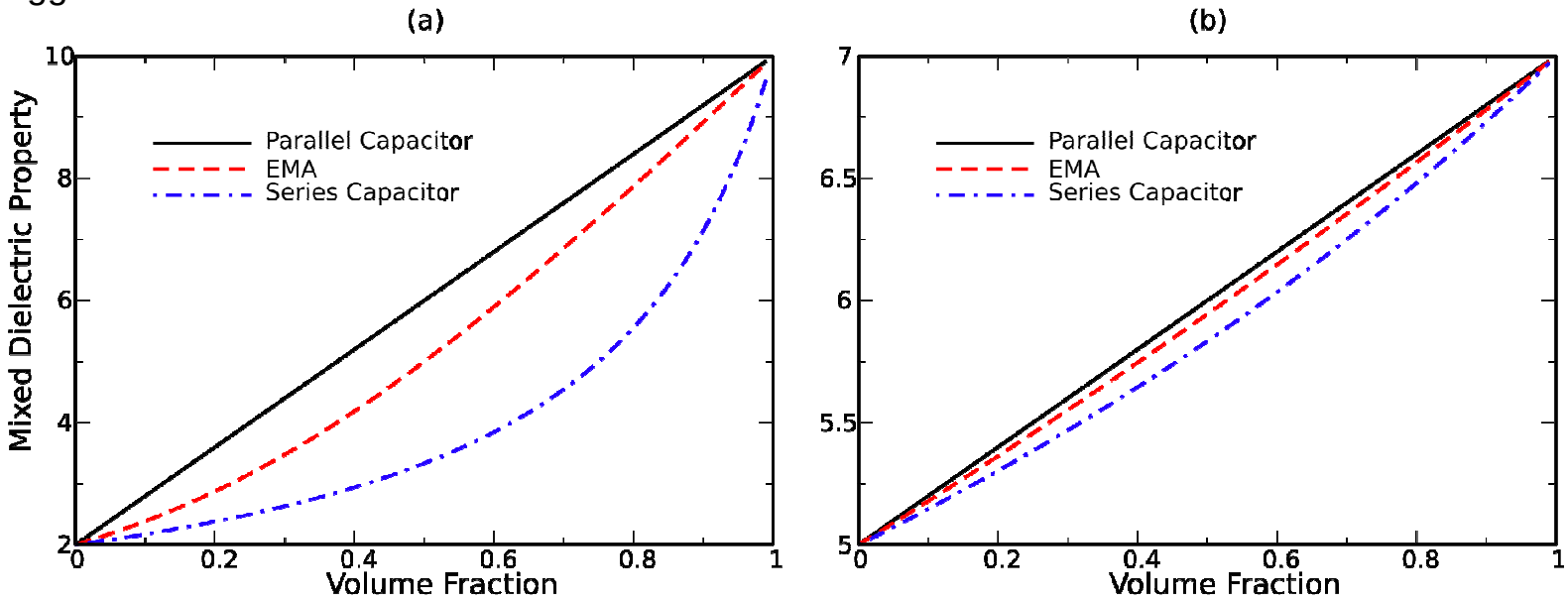
The Different Directions Of The SWCNT

- Have Different Connectivity



Sensible Approach:

- Parallel Capacitor In The Axial Direction
- Bruggeman Ema In The Radial Direction



$$\frac{1}{\epsilon} = \sum_i \frac{\phi_i}{\epsilon_i}$$

Series Capacitor

$$\sum_i \phi_i \frac{\epsilon_i - \epsilon}{\epsilon_i + 2\epsilon} = 0$$

Bruggeman EMA

$$\epsilon = \sum_i \phi_i \epsilon_i$$

Parallel Capacitor

All Models Converge For Very Small Optical Contrast

Multiwalled CNTs By "Mixing" The SWCNTs

Example: Making MWCNTs out of SWCNT components.

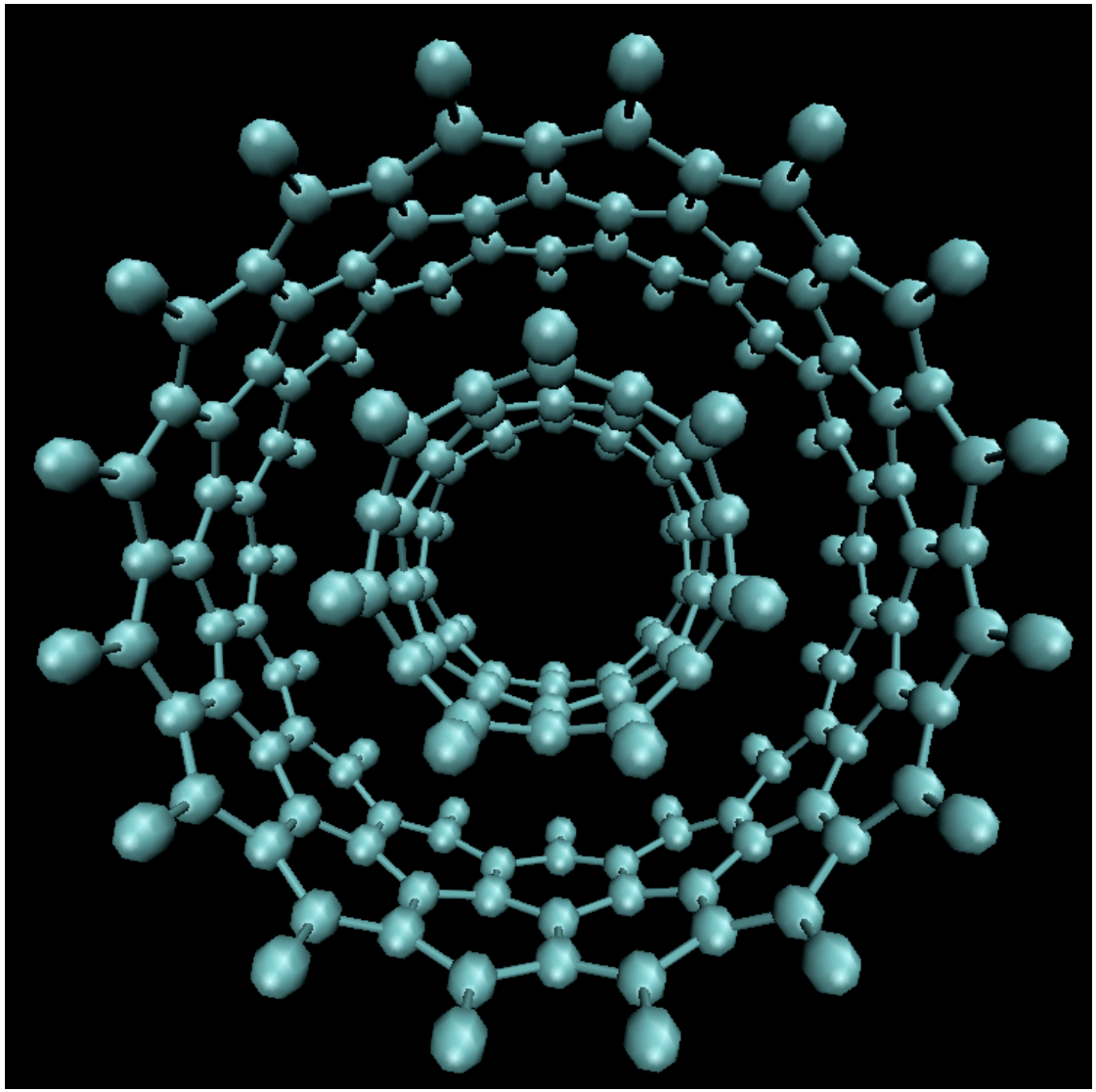
Consider A
[16,0,s + 7,0,s]
ZigZag MWCNT

[16,0,s] with

[7,0,s] inside

Compare Direct
LDA Calculation
Of MWCNT

With Mixing Of
[16,0,s] & [7,0,s]
Optical Properties



Multiwalled CNTs By "Mixing" The SWCNTs

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Compare Direct LDA Calculation Of MWCNT

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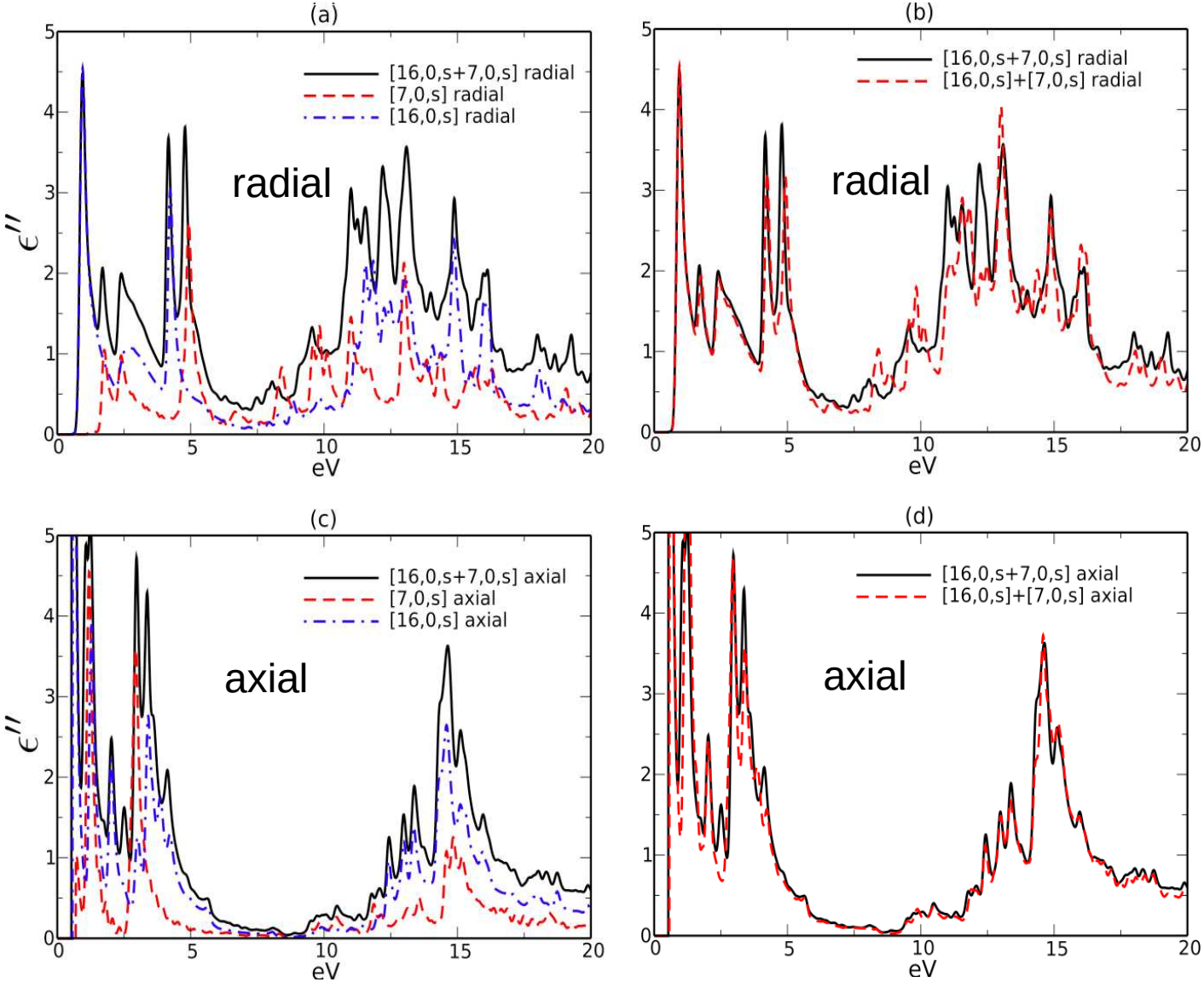


Datamining 60 CNTs: Trends And Classification

The miracles of science™

Datamining: ab initio Optical Properties Of 60 CNTs

We Have ab initio Optical Properties Of 60 SWCNTs

- And Numerous MWCNTs

Consider The 5 CNT Types

- "Metals": Armchair, Zigzag, Chiral
- Semiconductors: Zigzag, Chiral

How To Understand Trends In vdW-Ld Interactions?

Explore Trends With CNT Radius & Chirality

- Dielectrophoresis Experiments Have Already Shown A Correlation
  - Of Interaction Energy With SWCNT Diameter[1]

What Is A "Metal"?

From Band Structure Or Transport Perspective

- Want Electron Transport At 0 eV

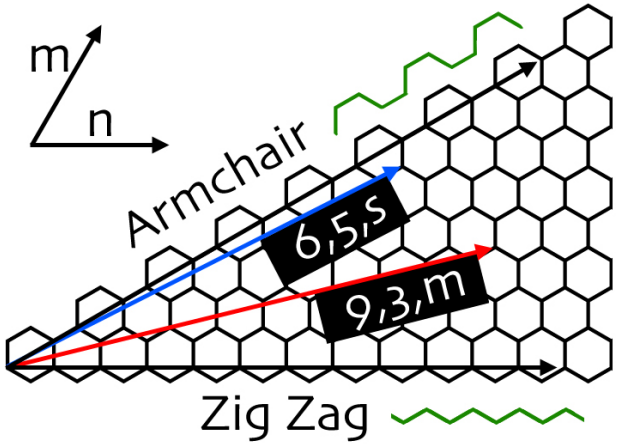
From Optical Property, Drude Metal Perspective

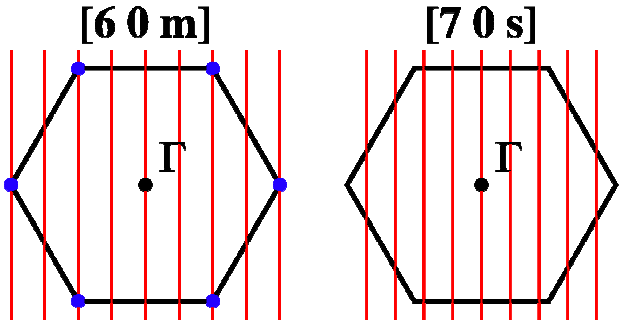
- Want Large Drude Metal Peak, Near 0 eV, In Axial Direction

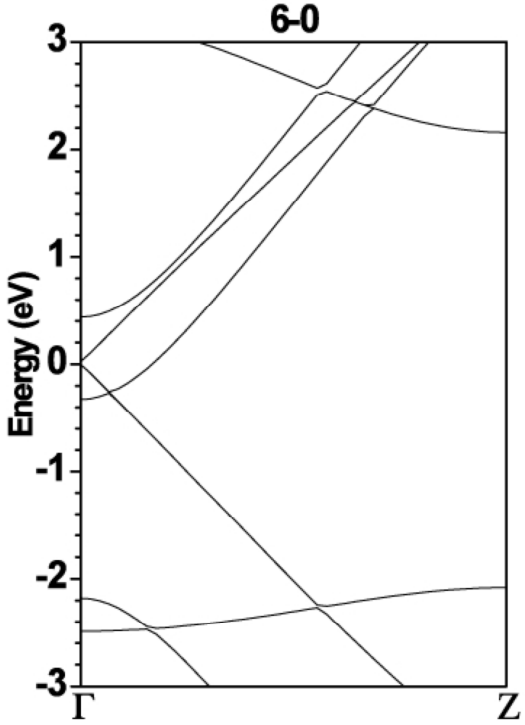
1. H. Peng, N. T. Alvarez, C. Kittrell, R. H. Hauge, H K. Schmidt, **J. Am. Chem. Soc.** 2006, 128, 8396-8397

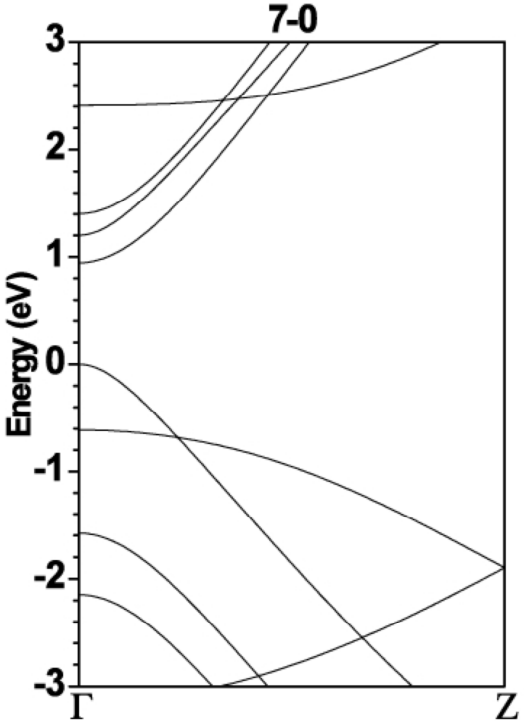
From [n,m] to Band Structure

SWCNTs: Small Difference In Chirality, Big Changes In Observable Properties









Small [n,m] Change Determines XYZ, Cutting Lines, Band Structure, ε'', vdW-Lds, Hamaker Coefficients, And Total Energies.

P. Lambin, **C. R. Phys**. 4, 1009 2003.

A New Classification

Many SWCNT Classifications Schemes Exist But…

- Tend To Focus On Bandgap Region 0-5 eV
- Primarily Concerned With Electronic Conduction

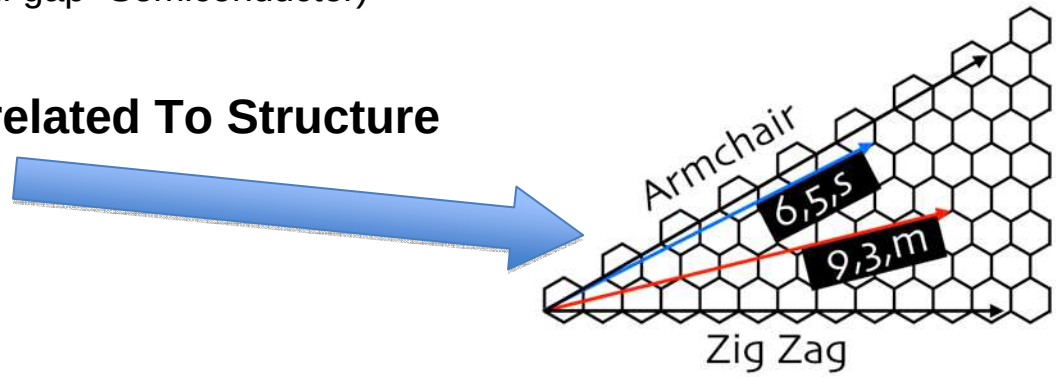
vdW-Ld Interactions Equally Dominated By 5-30+ eV Range

0-5 eV Range Is Highly Correlated To Electronic Conduction

- (i. e. Metal, Semiconductor, Or “Small-gap” Semiconductor)

5-30 eV Range Is Highly Correlated To Structure

- (i. e. Zigzag Vs. Armchair Vs. Chiral)



Merge The Two: The vdW-Lds Classification =

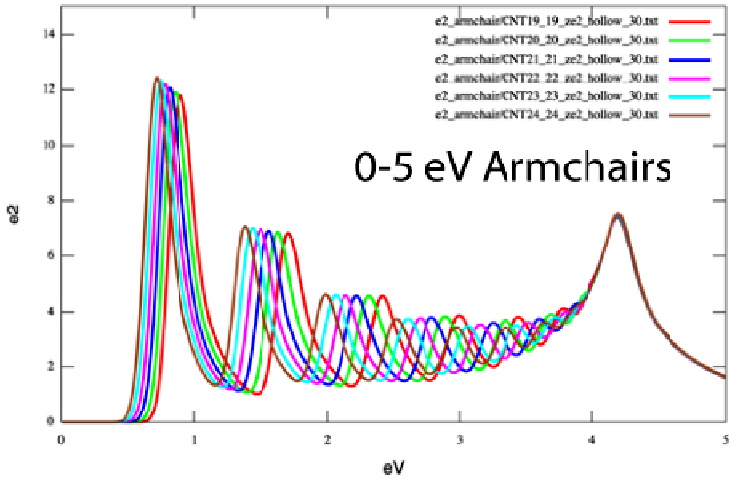
Ec Conduction (Metal Vs. Semiconductor) +

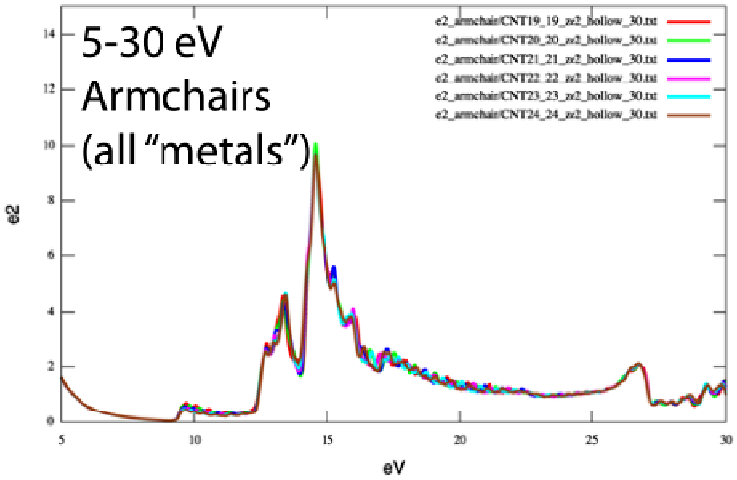
Structure (Armchair, Zigzag, Or Chiral).

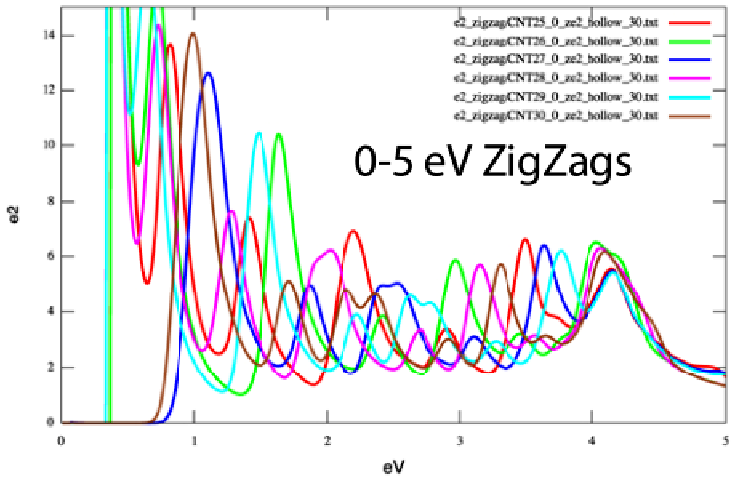
ZigZag vs. Armchair SWCNTs

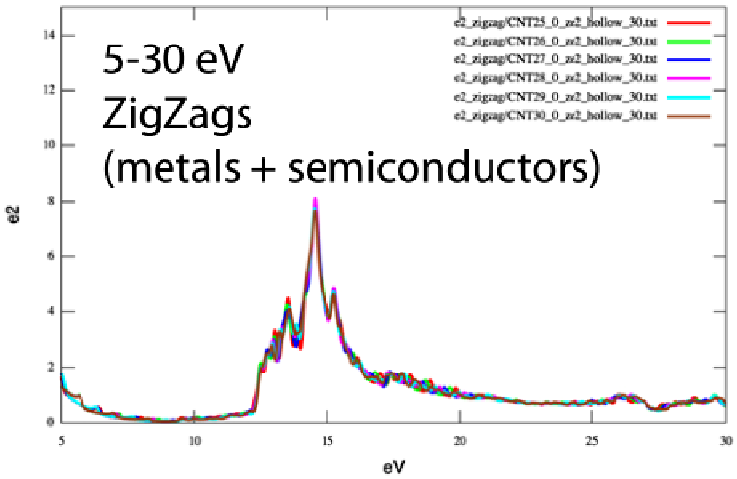
Notable Trends Both Within And Between Classes From 0-5 eV

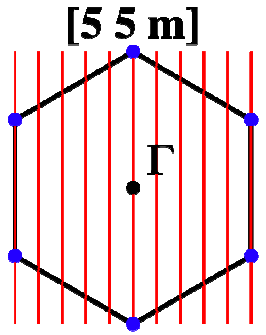
Notable Trends Between Classes From 5-30 eV

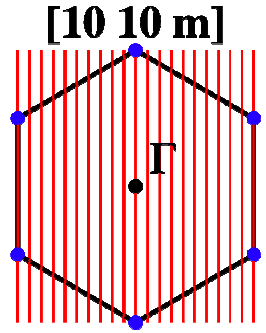


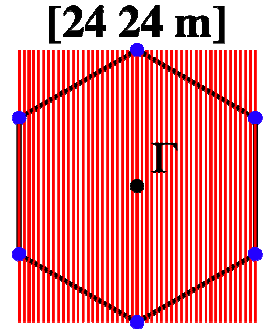




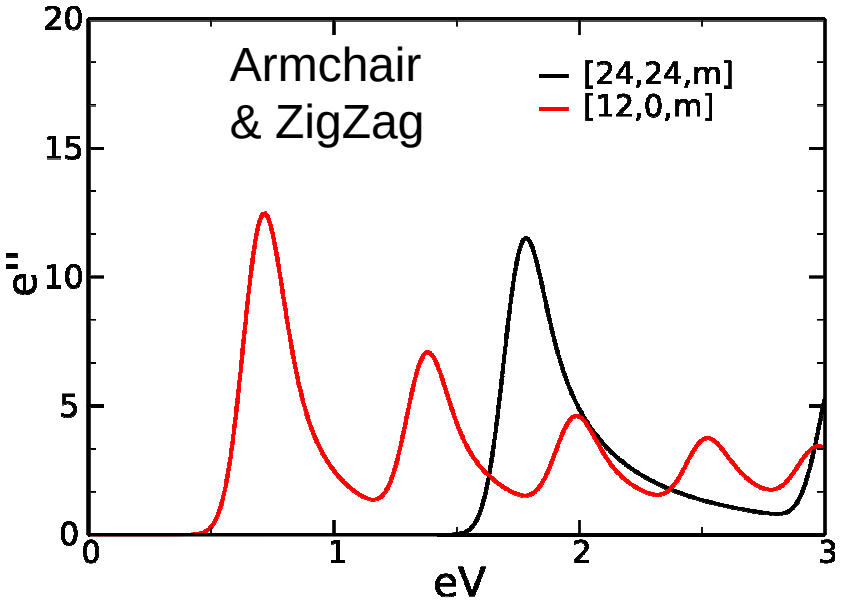


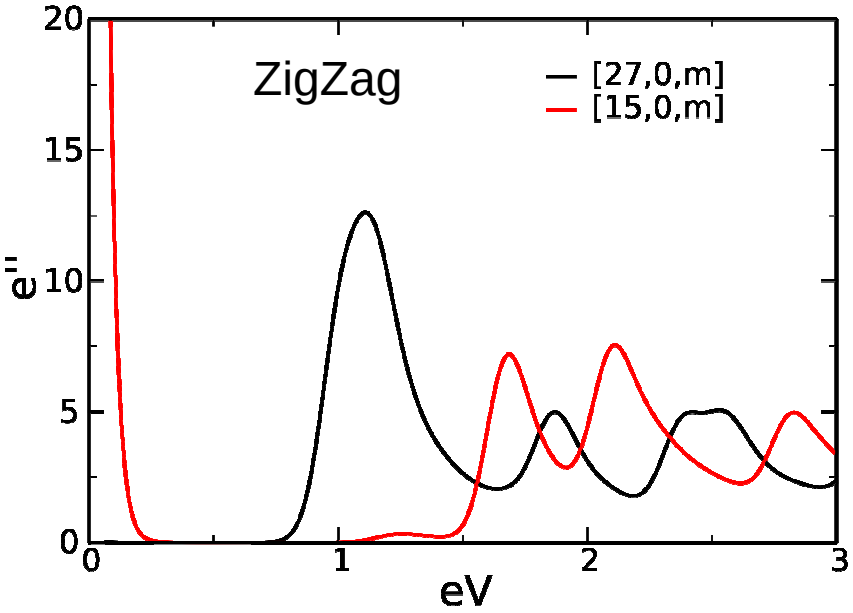


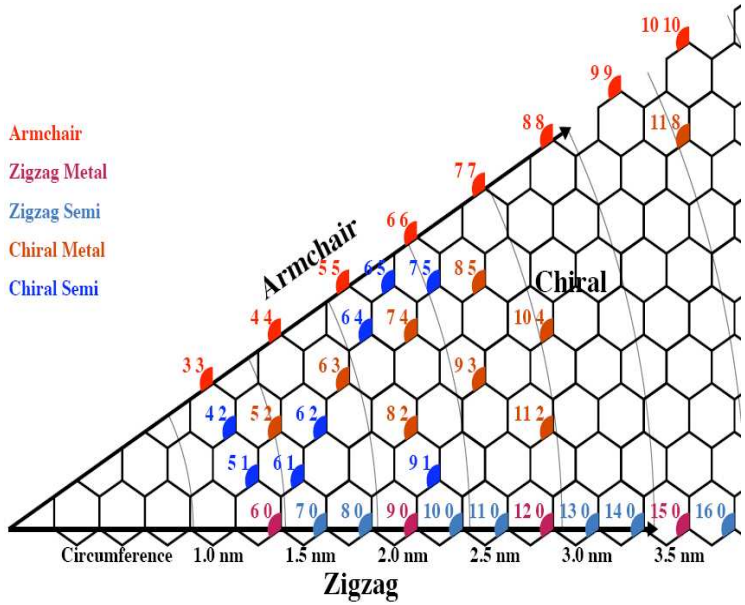


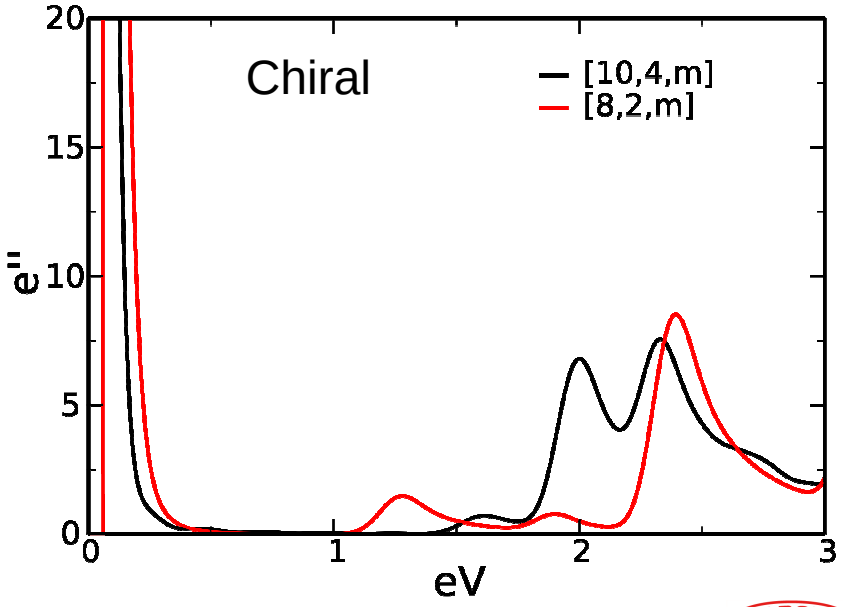


“Drude” Metal Peaks vs. Classification Type

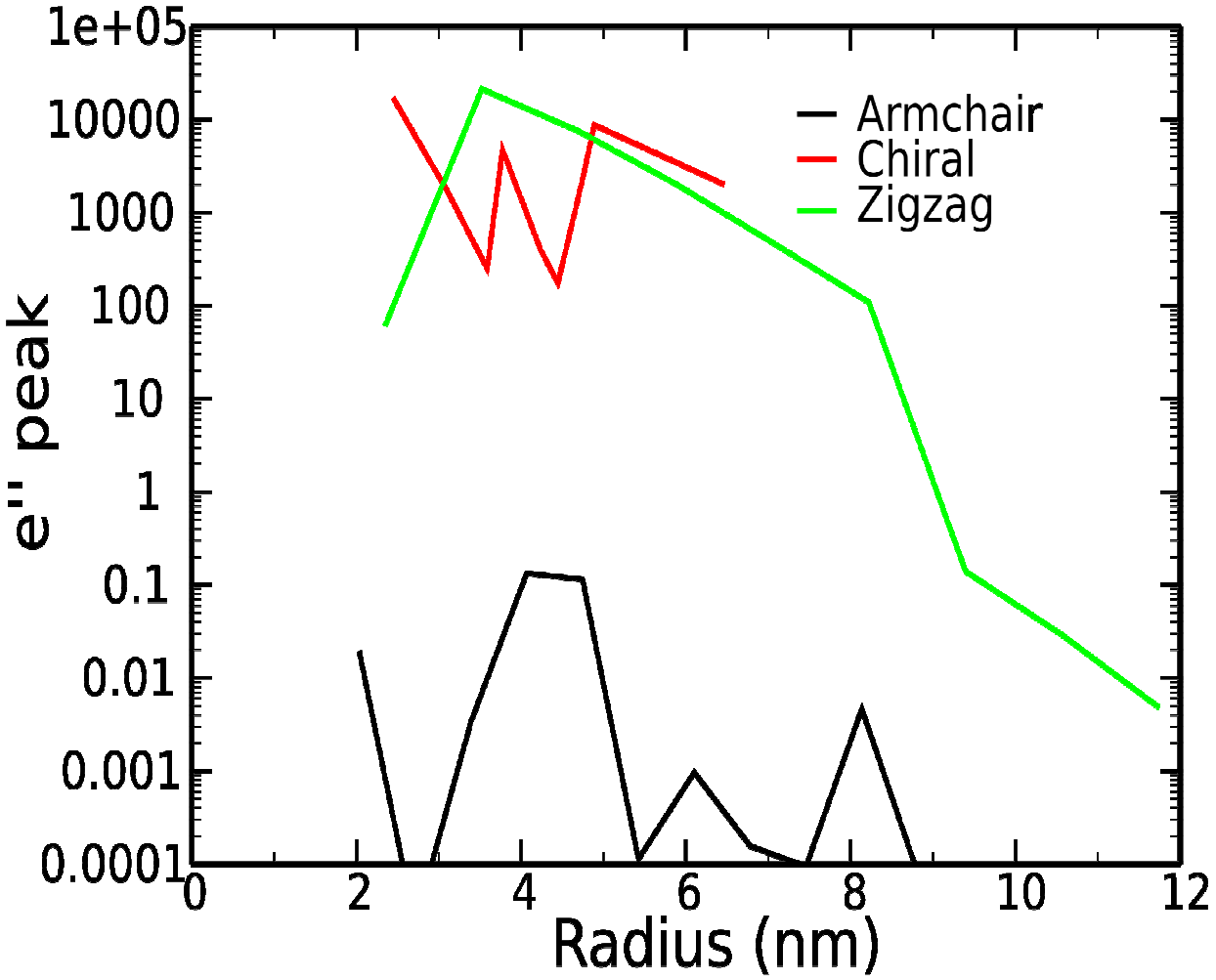








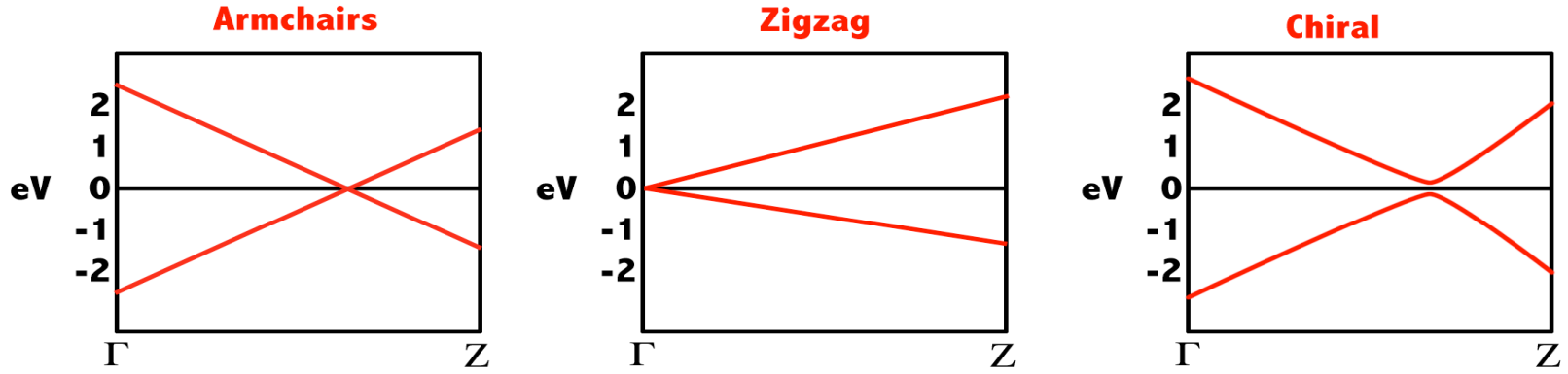
“Drude” Metal Peak Height vs. CNT Radius



Classification Of CNT Types: Optical Perspective

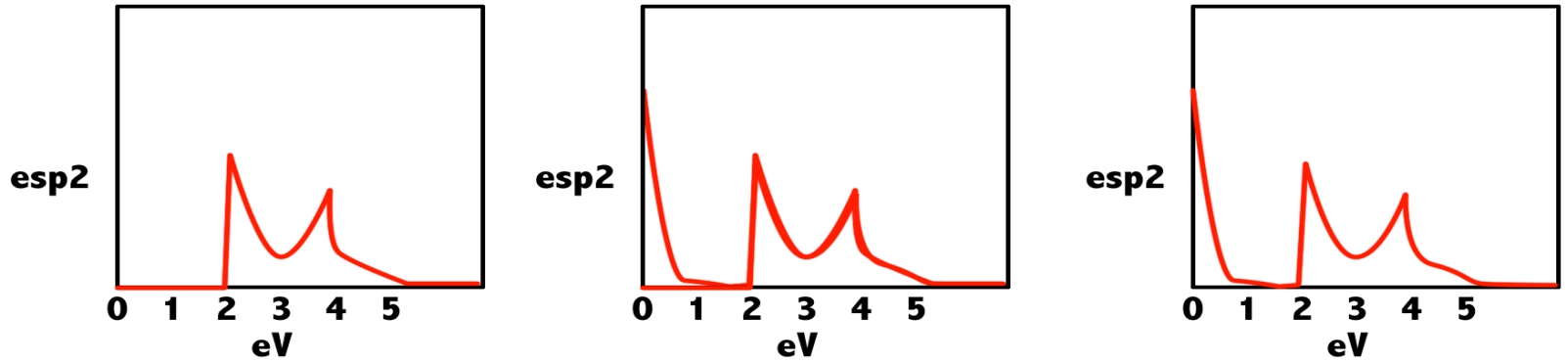
Comparing the different "Metals"

DOS



No eps2 spike | Sometimes eps2 spike | Always eps2 spike

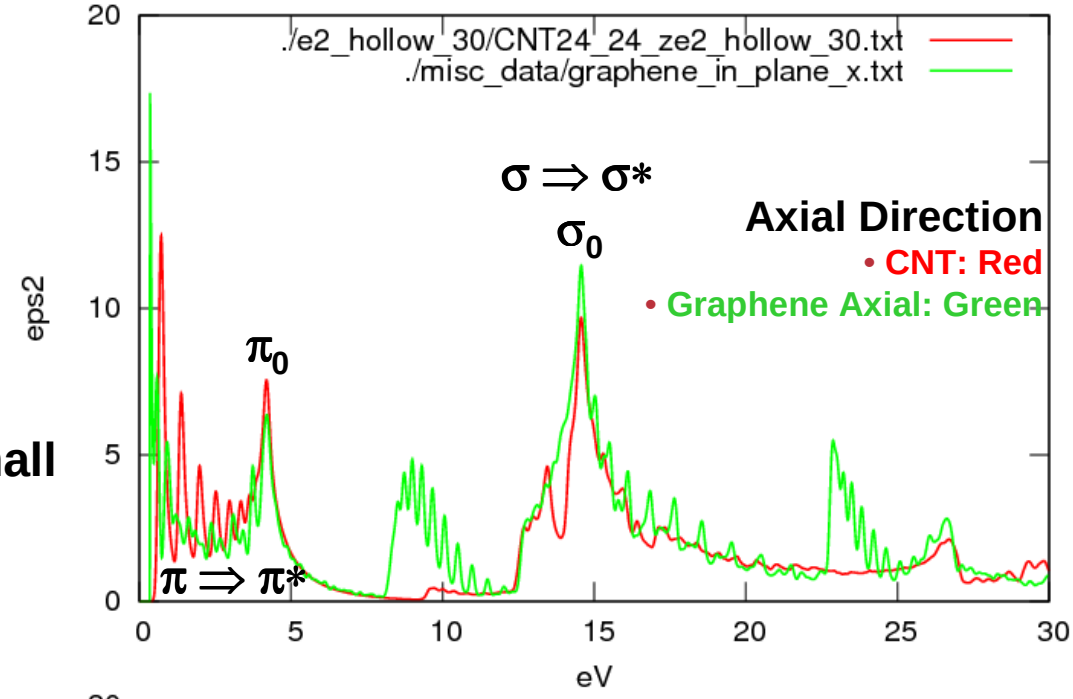
Interband Optical Properties

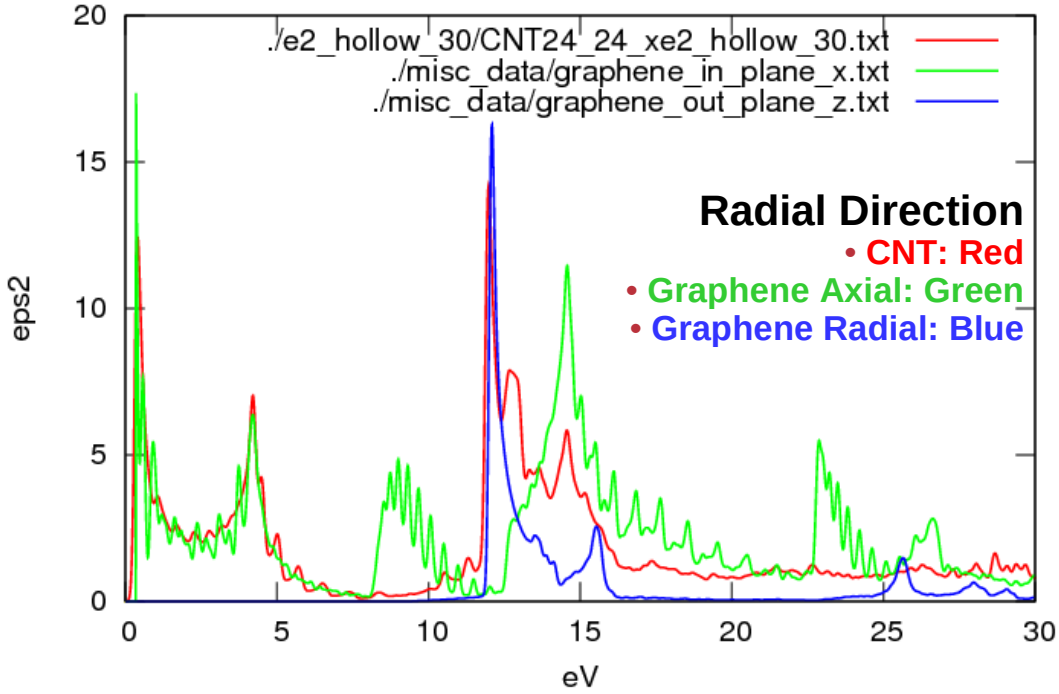


Band Crossing	Band Touching	Band Gap
No Drude Metal Peak	Drude Metal Peak?	Drude Metal Peak
Semi-metal	Metal or Semi-metal	Small Gap Metal

Electronic Conduction And Optical Perspectives: Confusing Terminology & Classifications

Armchair "Metal" CNTs: Semi-metals





Animations: Large Diameter To Small

- Have [3,3,m] to [24,24,m]

Large Diameter

- Simple Trending Behavior

More Bond Strain/Re-hybridization

- At Small CNT Diameters

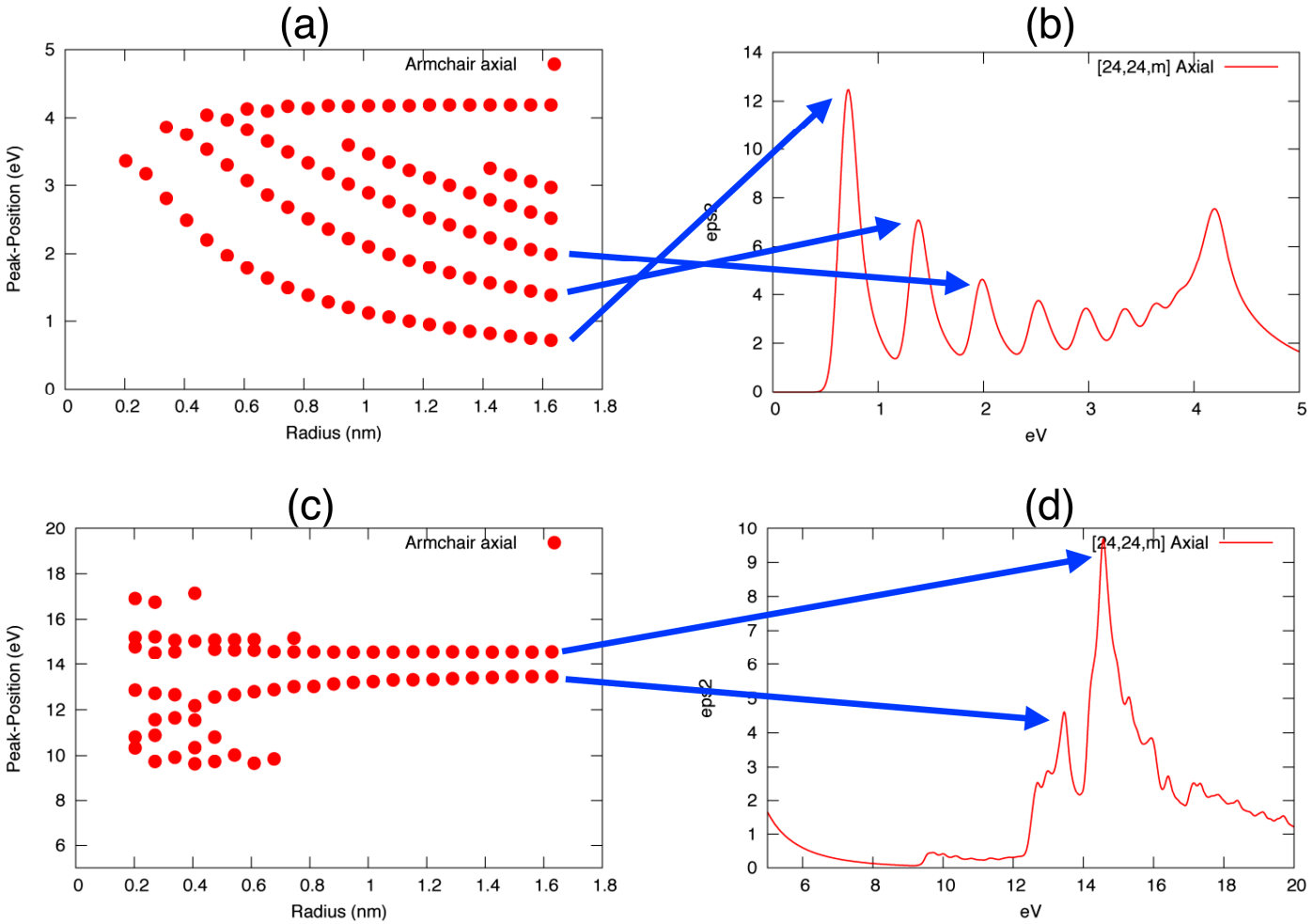
Axial Direction: No Drude Peak

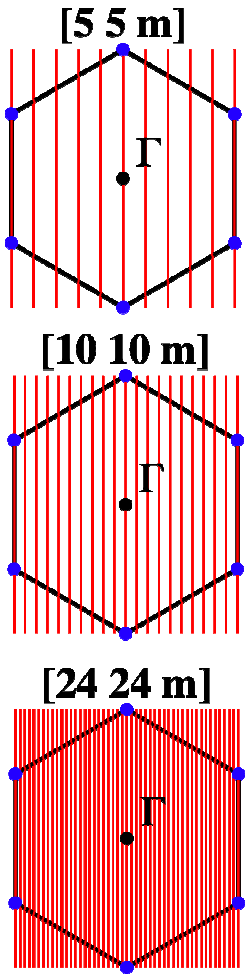
- Semi-metal, Not Good Metal

Armchair "Metals" Trend Stability

SWCNTs Below A 0.6-0.8 Nm Radius Break From Trends

- Exhibit New Features



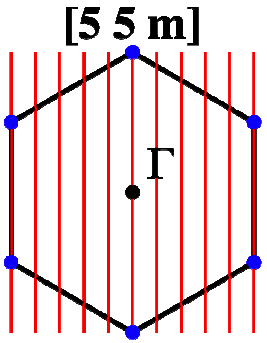


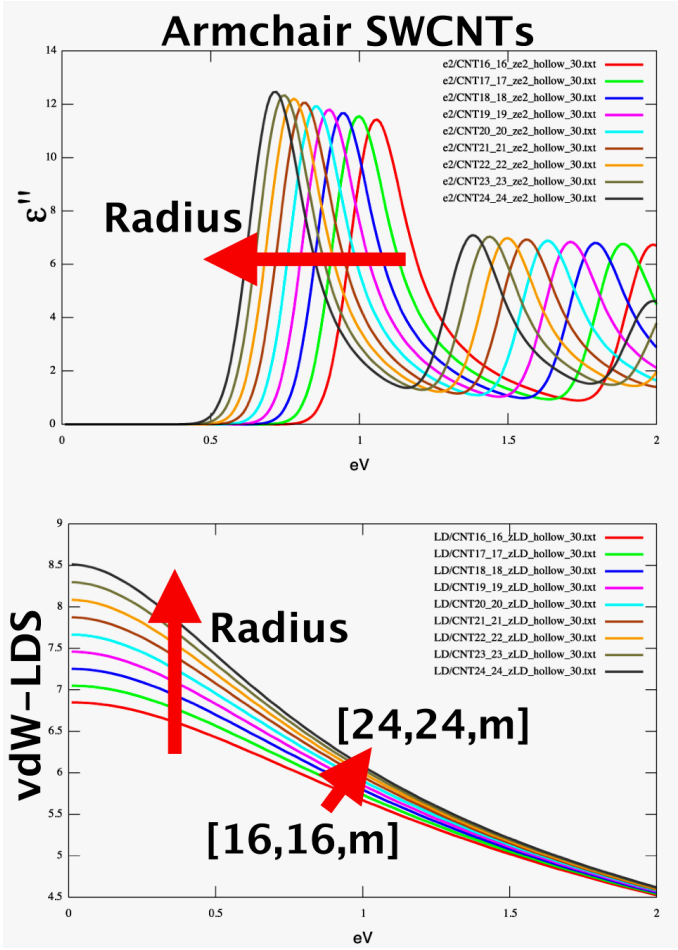
Greater Variation = Greater Ability For Chirality Specific Interaction

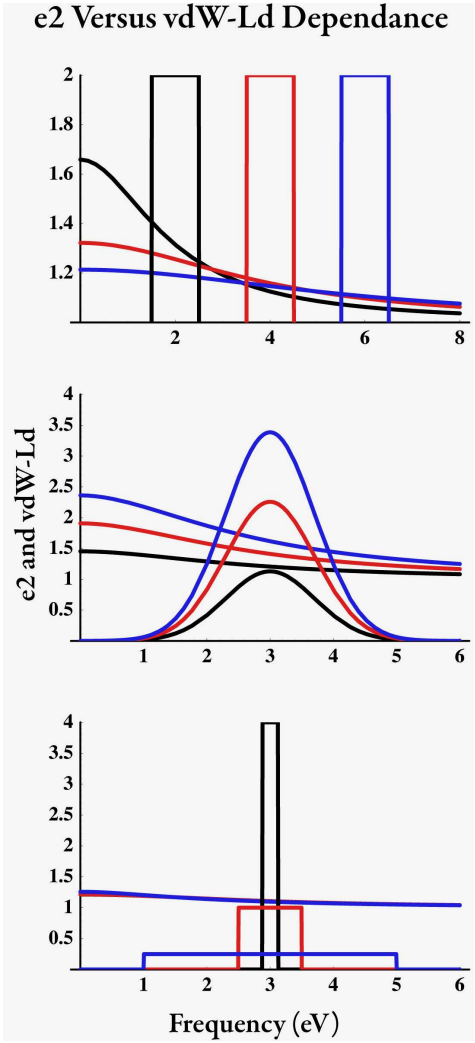
SWCNTs 2: Armchair Example ε'' to vdW-LD Spectra

Manipulations Or Variations In ε'' Have Systematic Effects On vdW-Ld Spectra

SWCNTs Have Known Band Gap Variations With Classification And Radius



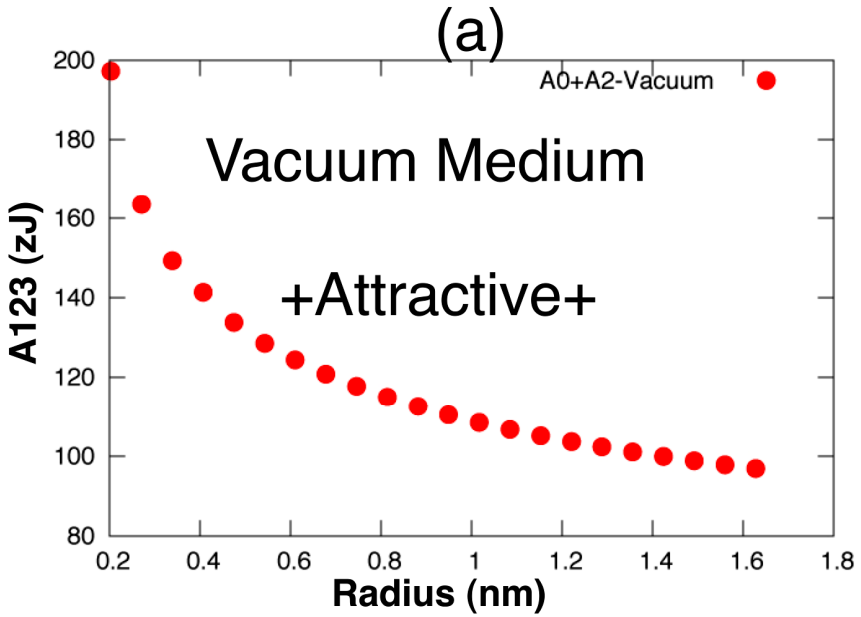


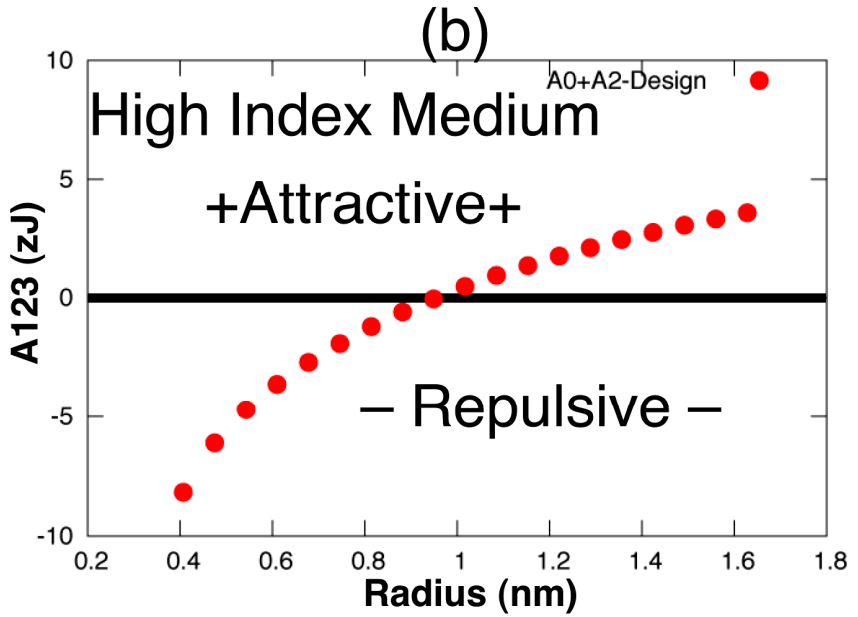


$$\epsilon(i\xi) = 1 + \frac{2}{\pi}\int_0^\infty \frac{\epsilon''(\omega)d\omega}{\omega^2+\xi^2}$$

Armchair Example of System Design (Buoyancy)

System: Bare SWCNT + Polystyrene Substrate + High Index Medium





A Critical Radius Of Attractive/Repulsive Divide

Changing The Index Can Change The Critical Radius Location

Multi Stage Experiments CouLd Create Mono-disperse Populations

More Parameters To Explore (Surfactants, Mwcnts, Etc.)

Conclusions

van der Waals–London Dispersion Interactions Of Carbon Nanotubes Requires

- ab initio Optical Properties From Band Structures
- Non-Plane Parallel vdW-Ld Development

Solid Cylinder Lifshitz Formulation

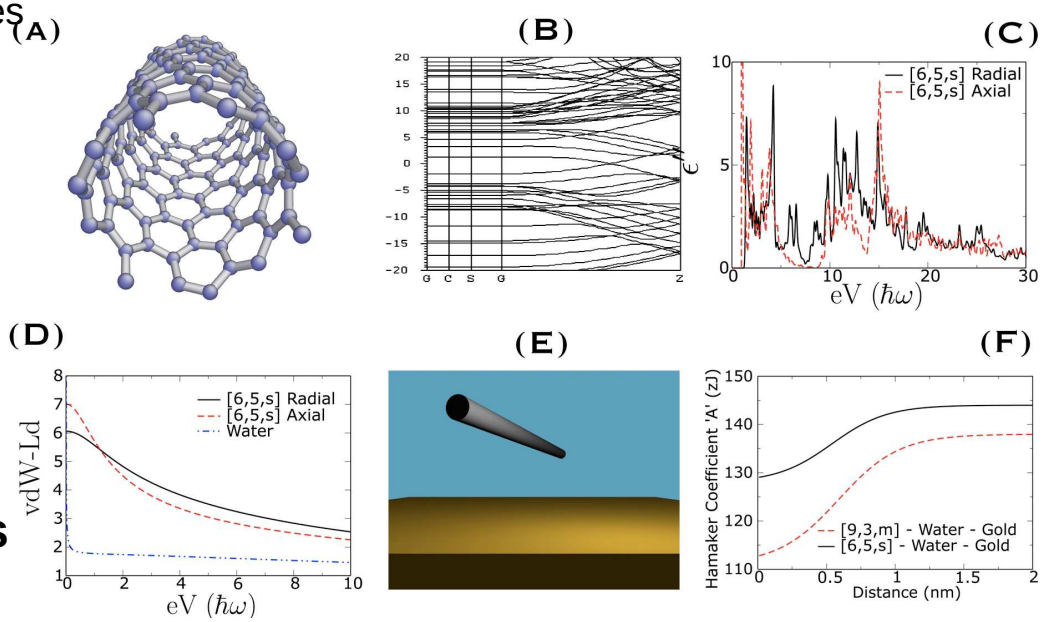
- Forces and Torques

CNT Optical Properties Differ

- Axial versus Radial
- $\pi \Rightarrow \pi^*$, $\sigma \Rightarrow \sigma^*$ Transitions

Strong Dispersion Torques & Forces

- Optical Anisotropy γ And Optical Contrast Δ



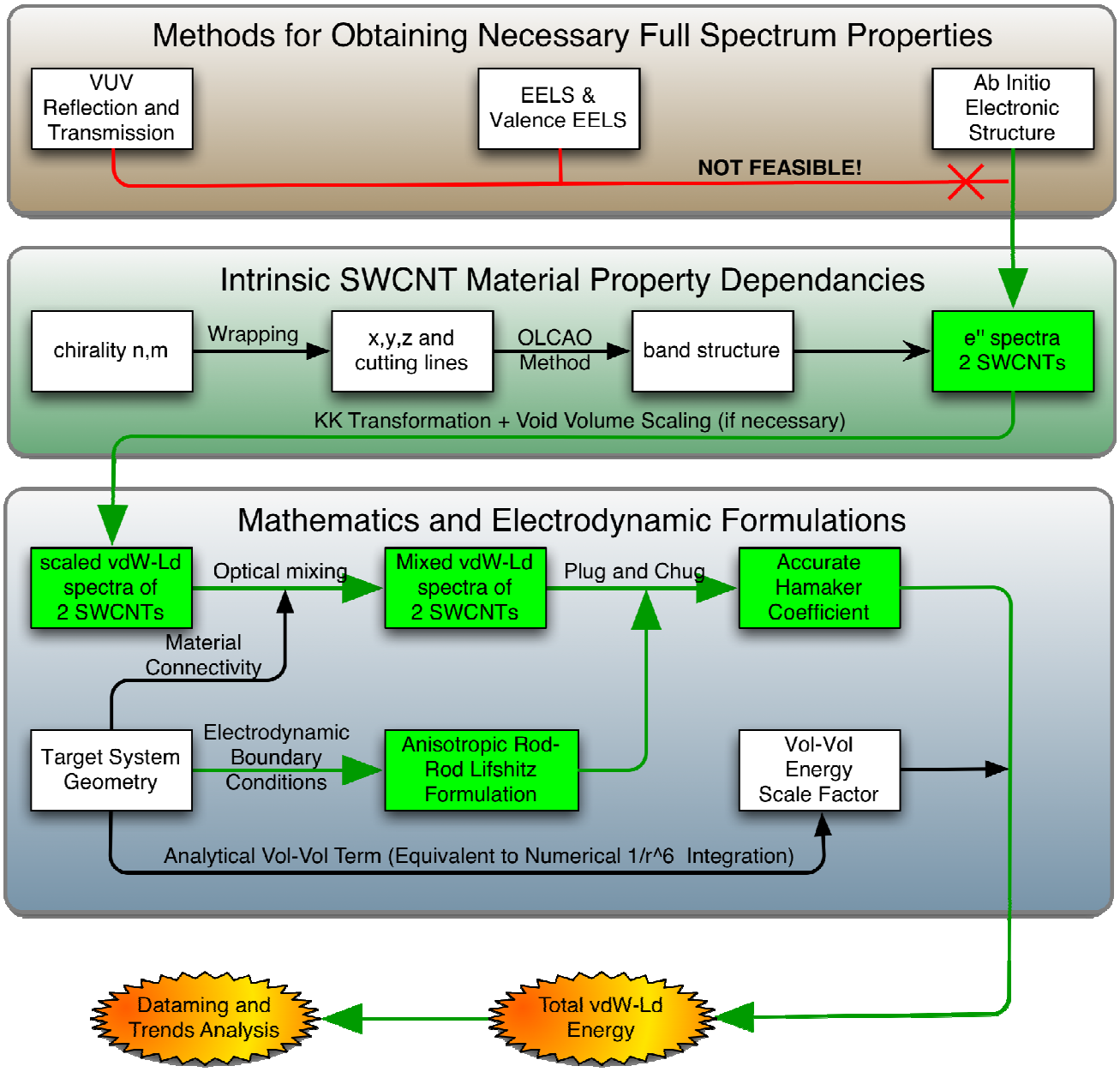
vdW-Ld Of CNTs Vary With

- Type: Armchair, Zigzag, Chiral
- Character: Drude Metal, Semi-metal, Small Gap Semiconductor, Semiconductor

Each CNT Chirality $\Rightarrow$ Unique Properties And Interactions

Anisotropic vdW-Ld Interactions Provide A Method

- **For CNT Separation By Type And Chirality**
- **For Mutual Alignment Of CNTs**

Conclusions Visually

Status of a SWCNT vdW-Ld Calculation After We Introduced Spectra Mixing