New Perspectives on London Dispersion Interactions and Hamaker Coefficients:

Dispersion Energy Of Graded Interfaces And Dispersion Driven RE Segregation

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Spectroscopy

- K. I. Winey (UPenn)
- G. L. Tan (UPenn)
- M. K. Yang (DuPont)
- M. F. Lemon (DuPont)
- D. J. Jones (DuPont)

Dispersion Interactions

- L. K. Denoyer (Deconvolution.com)
- V. A. Parsegian (NIH)
- R. Podgornik (Slovenia)

Electronic Structure Calculations

- Wai Yim Ching (Univ. Missouri–Kansas City)

$SrTiO_3$

- K. van Benthem (ORNL)
- M. Ruhle (MPI-Stuttgart)
- C. Elsasser (MPI-Stuttgart)
- Manfred Rühle
- Max Planck - Stuttgart

Si_3N_4

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- Raphaelle Satet (Univ. of Karlsruhe)
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PS, P(S-MMA), PMMA, PET

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Polysilanes

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This work was partially supported by NSF award DMR-0010062 and the European Union under contract G5RD-CT-2001-00586

History of The London Dispersion Interaction

T. Young (1805)

- **An Essay on the Cohesion of Fluids**

J. W. Gibbs (1875)

J. D. van der Waals (1893)

- Theory of Capillarity

Sellmeier (1872)

- **Regarding the Sympathetic Oscillations Excited in Particles by Oscillations of the Ether and Their Feedback to the Latter, Particularly as a Means of Explaining Dispersion and its Anomalies**

Maxwell’s Equations

- Oliver Heaviside

R. de L. Kronig, (1926)

- On The Theory of Dispersion of X-Rays

F. London (1930)

- General Theory of Mol. Forces
- Induced Dipoles

Hamaker (1937)

- Hamaker Constant

Casimir (1948)

- Attraction of 2 Conducting Plates
- QED - Casimir Force

Lifshitz (1956)

- QED - General Theory
- With Retardation Effects

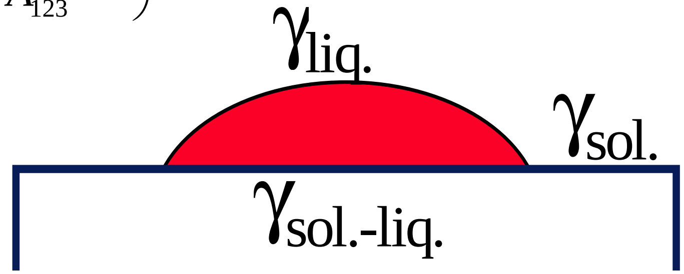
R. H. French, Journal of the American Ceramic Society, 83, 9, 2117-46 (2000).

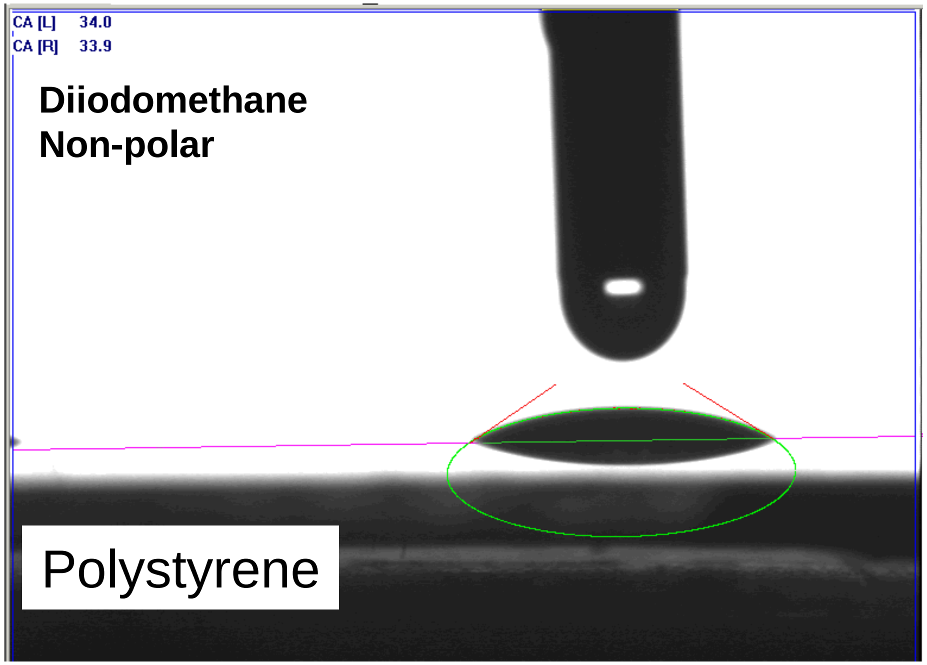
Dispersion Contribution to Surface Free Energy

vdW - London Dispersion Energy

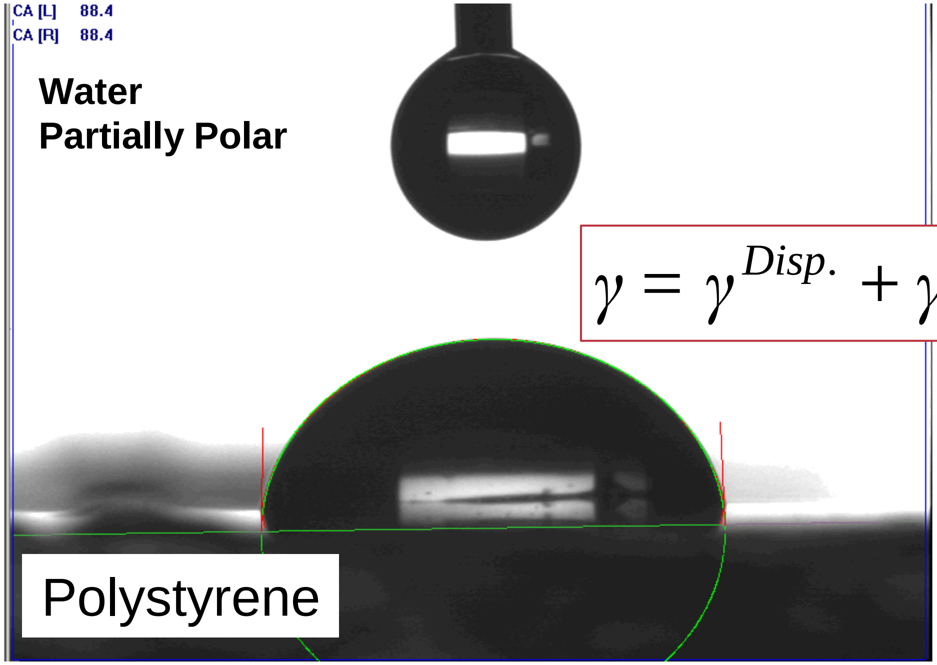
- Thermodynamic Free Energy Arising From
  - London Dispersion Interaction
- Dispersive Component Of Surface Free Energy

$$\theta = \arccos\left(\frac{A_{121}}{A_{123}} - 1\right)$$





Electrodynamic (vdW-LD) & Polar Interactions



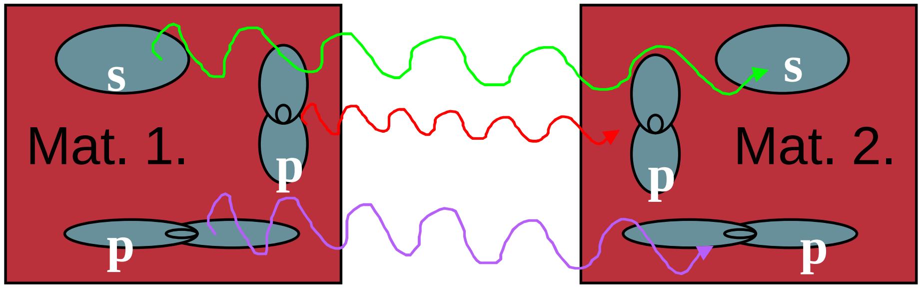
$$\gamma = \gamma^{Disp.} + \gamma^{Polar}$$

R. H. French, K. I. Winey, M. K. Yang, W. Qiu, **Aust. J. Chem.,60**, 251-63, (2007).

Introduction

van der Waals-London Dispersion Interactions

- Thermodynamic Free Energy



Arises From Oscillating Dipoles

- Interatomic Bonds of Elect. Struc.

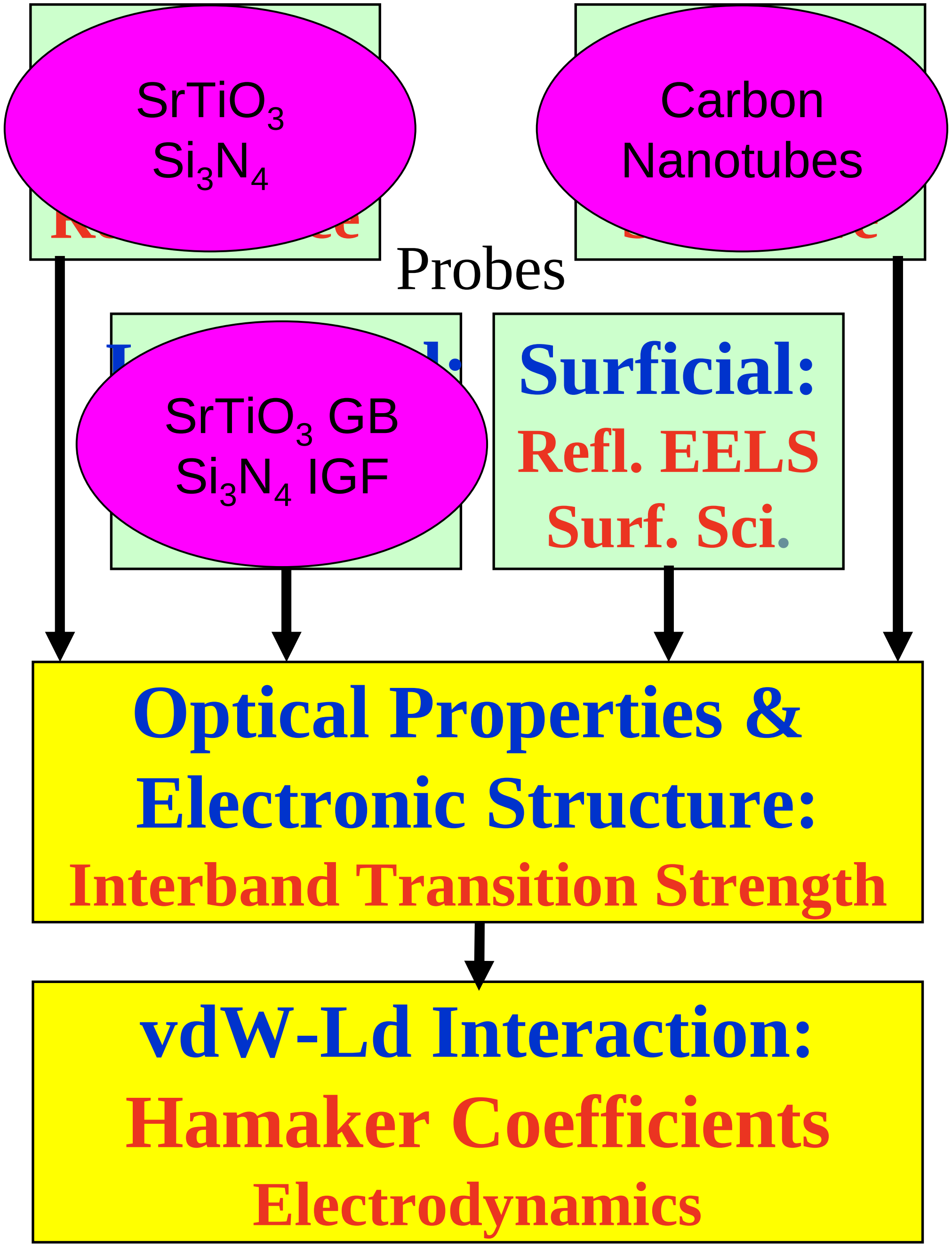
J_{cv}, ε” => London Disp. Spectra

A - Hamaker Constant

- Interaction Scaling Constant

F_{disp} - Dispersion Force

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



$SrTiO_3$
Si_3N_4

Carbon
Nanotubes

Probes

$SrTiO_3$ GB
Si_3N_4 IGF

Surficial:
Refl. EELS
Surf. Sci.

Optical Properties &
Electronic Structure:
Interband Transition Strength

vdW-Ld Interaction:
Hamaker Coefficients
Electrodynamics

Outline

Interfaces In Ceramics And vdW-Ld Interactions

Optical Properties And Electronic Structure

van der Waals – London Dispersion Interactions

1. vdW-Ld Energies Of Grain Boundaries in $SrTiO_3$

2. Role Of Retardation In Novel Wetting Phenomena

3. vdW-Ld Driven Rare Earth Segregation In RE-M-SiON: Si_3N_4

Conclusions

Interfaces In Ceramics

And The vdW-Ld Interaction

Atomically Structured Grain Boundaries

Nanostructured Amorphous Films

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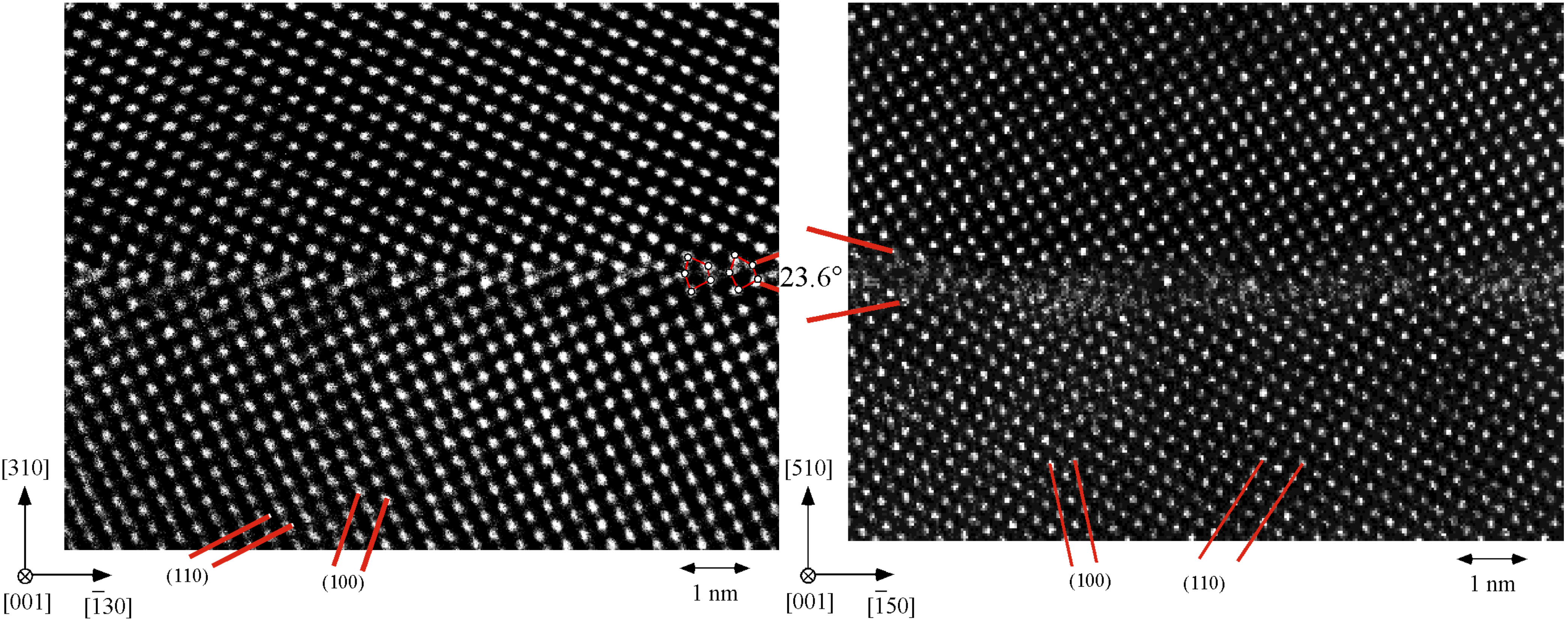
$SrTiO_3$:Fe Bi-crystals

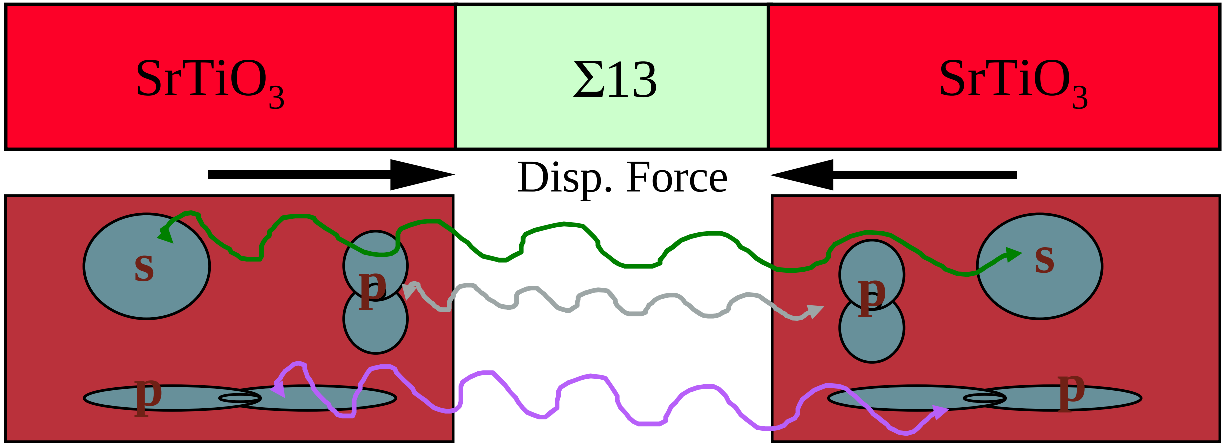
Σ 5 Boundary

- Atomically Structured

nΣ 13 Boundary

- Atomically Structured





IGF’s in Thick Film Resistors

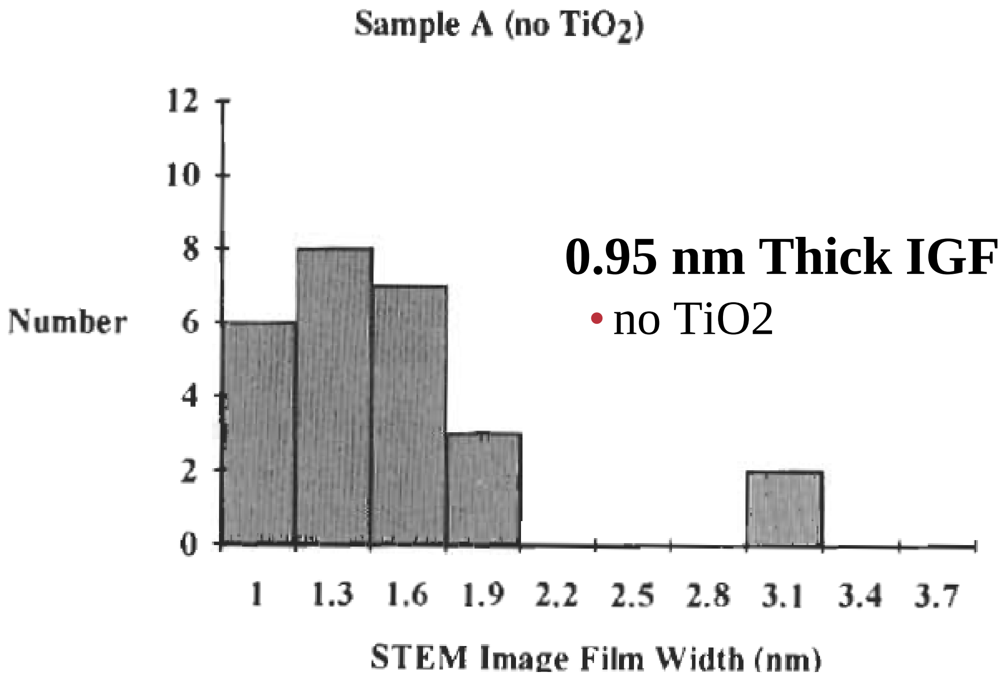
$Pb_2Ru_2O_7$ Conductor Particles

Separated by PbAl-Silicate

Intergranular Glass Films

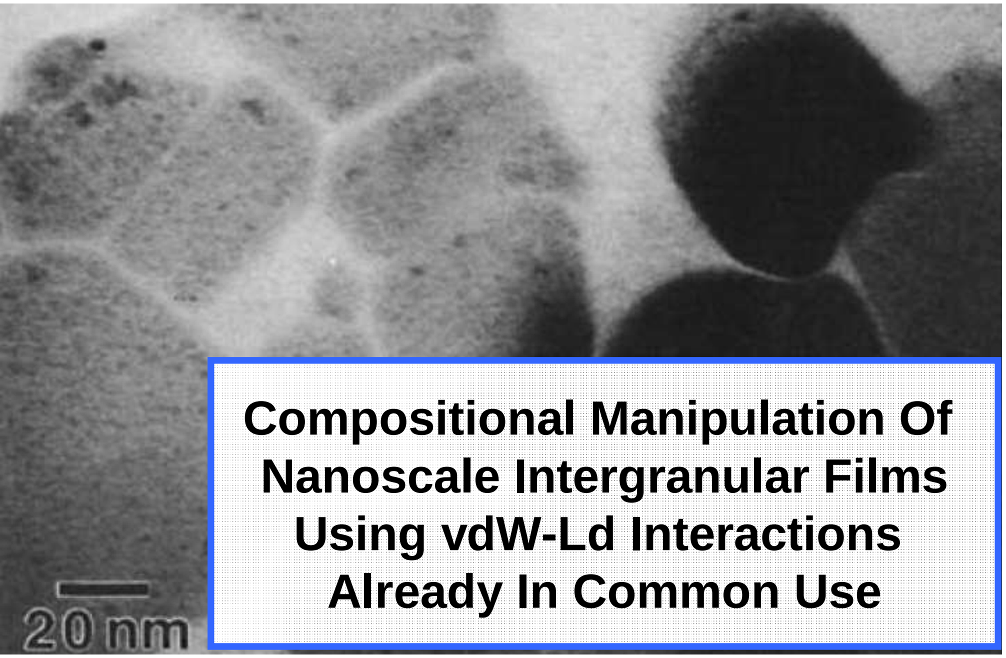
This TiO_2 Effect Arises From

- Ti Segregation To Grain Surfaces
- A 5 Layer Hamaker Configuration

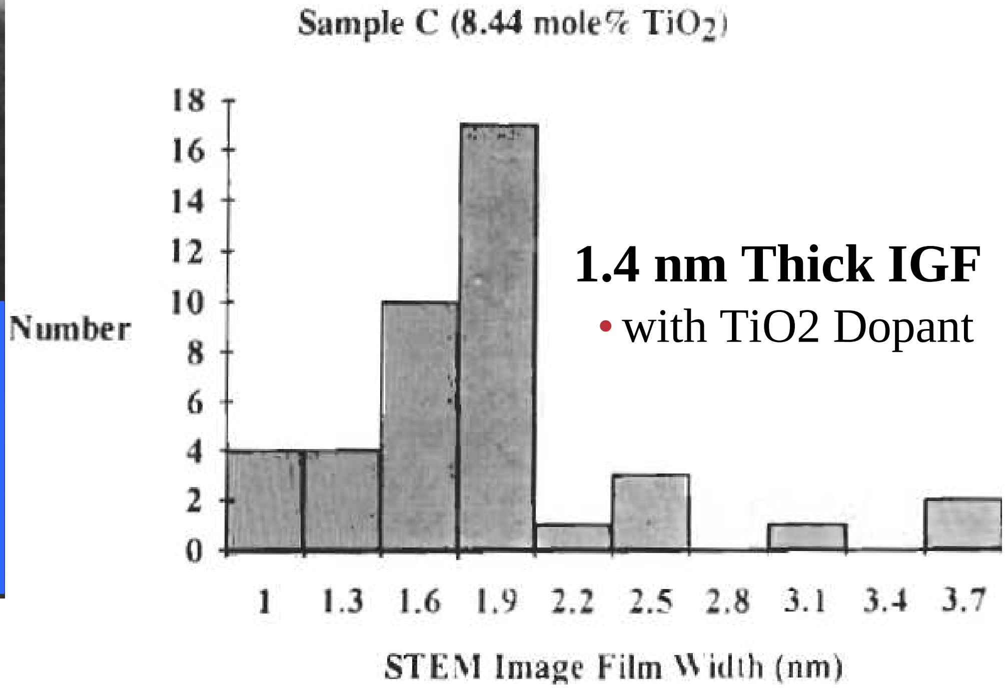


0.95 nm Thick IGF

- no TiO2



Compositional Manipulation Of Nanoscale Intergranular Films Using vdW-Ld Interactions Already In Common Use



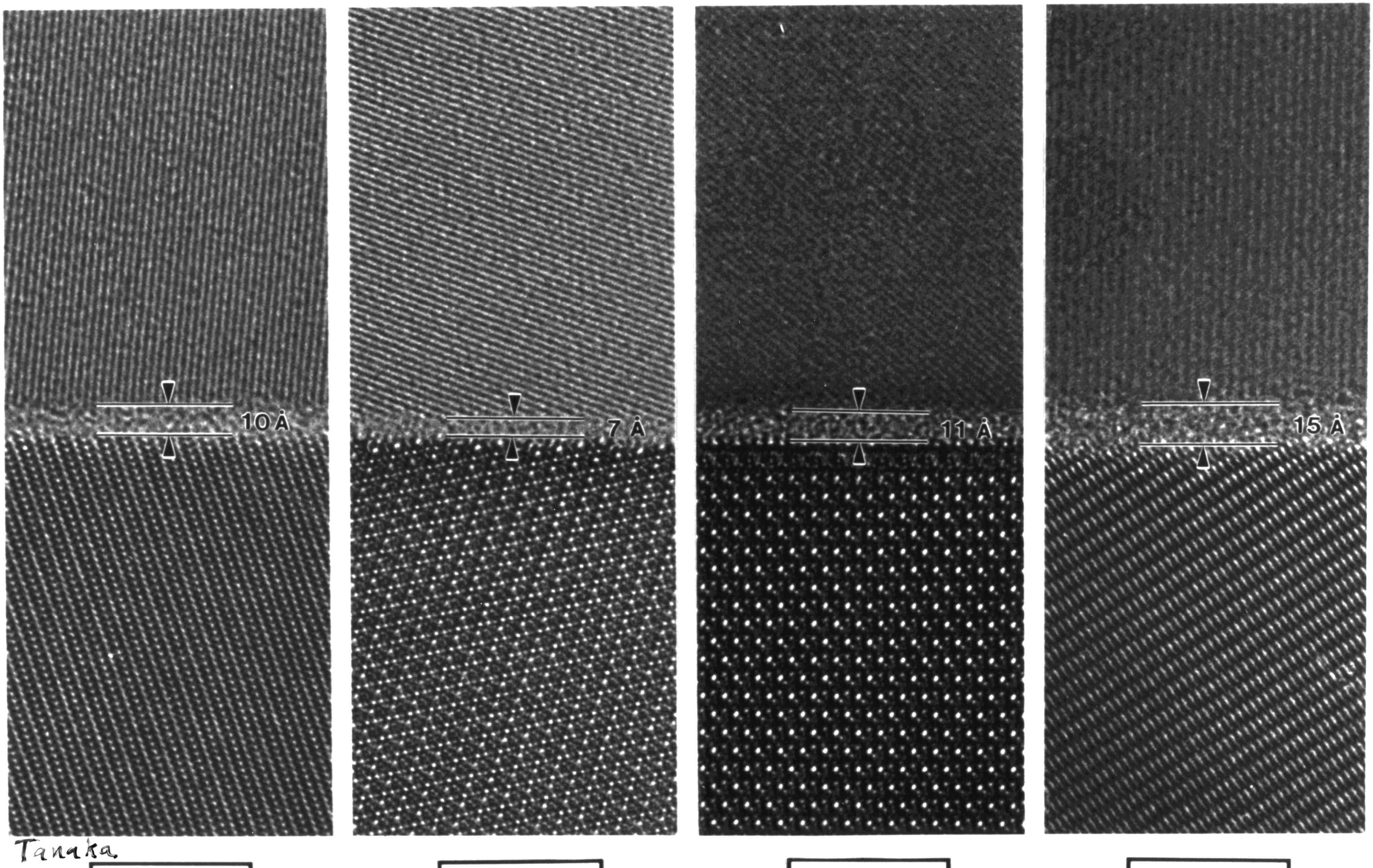
1.4 nm Thick IGF

- with TiO2 Dopant

Y. M. Chiang, L. E. Silverman, R. H. French, R. M. Cannon, J. Am. Ceram. Soc., 77, 1143-52, (1994).

Si_3N_4 : Nanostructured Amorphous Films

Equilibrium Intergranular Glassy Films



undoped 1.0 nm **80 ppm Ca** 0.7 nm **220 ppm Ca** 1.1 nm **450 ppm Ca** 1.5 nm

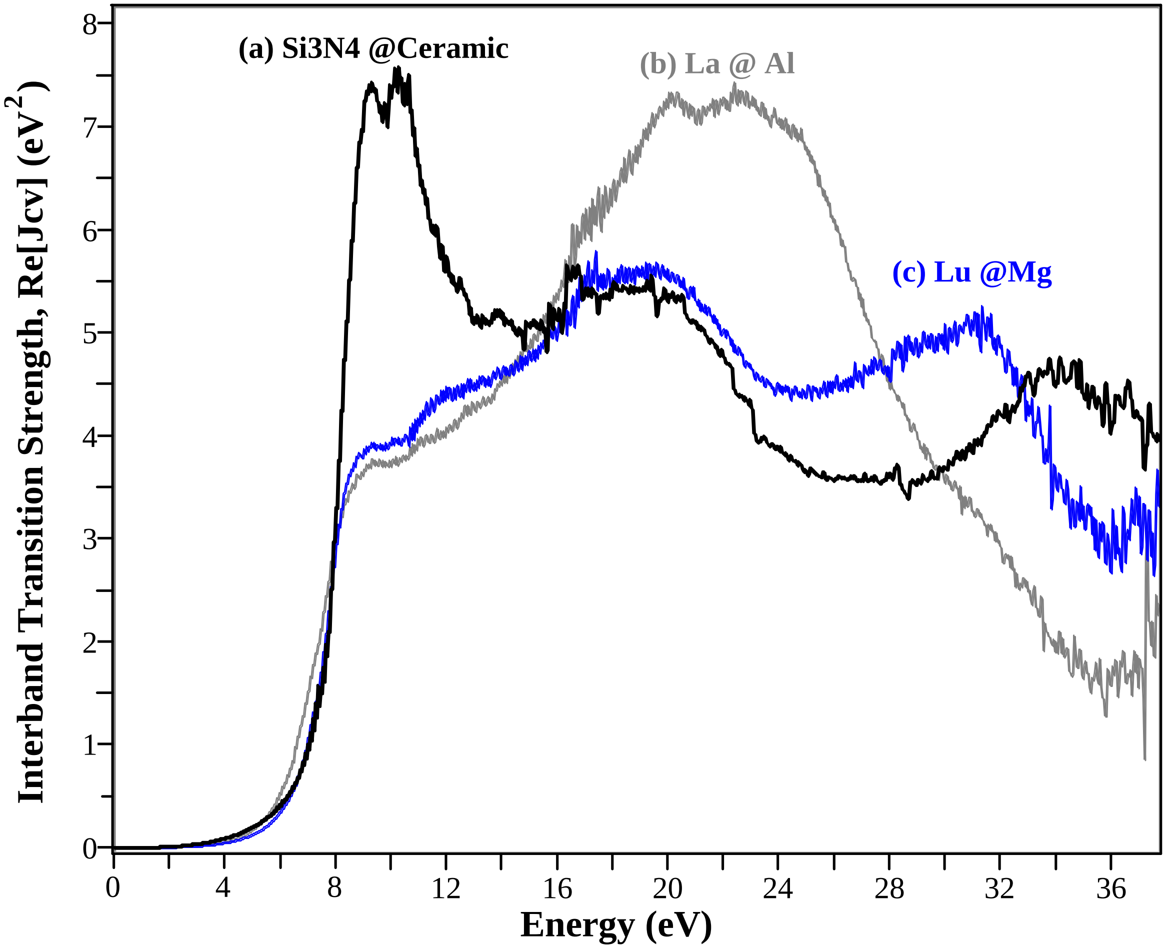
Properties Of Rare Earth-M-SiON:

Bulk SiON Glasses

- Al or Mg Family
- RE Dopants: Y, Lu, La, Gd

Jcv: Interband Transitions

- VUV Spectroscopy



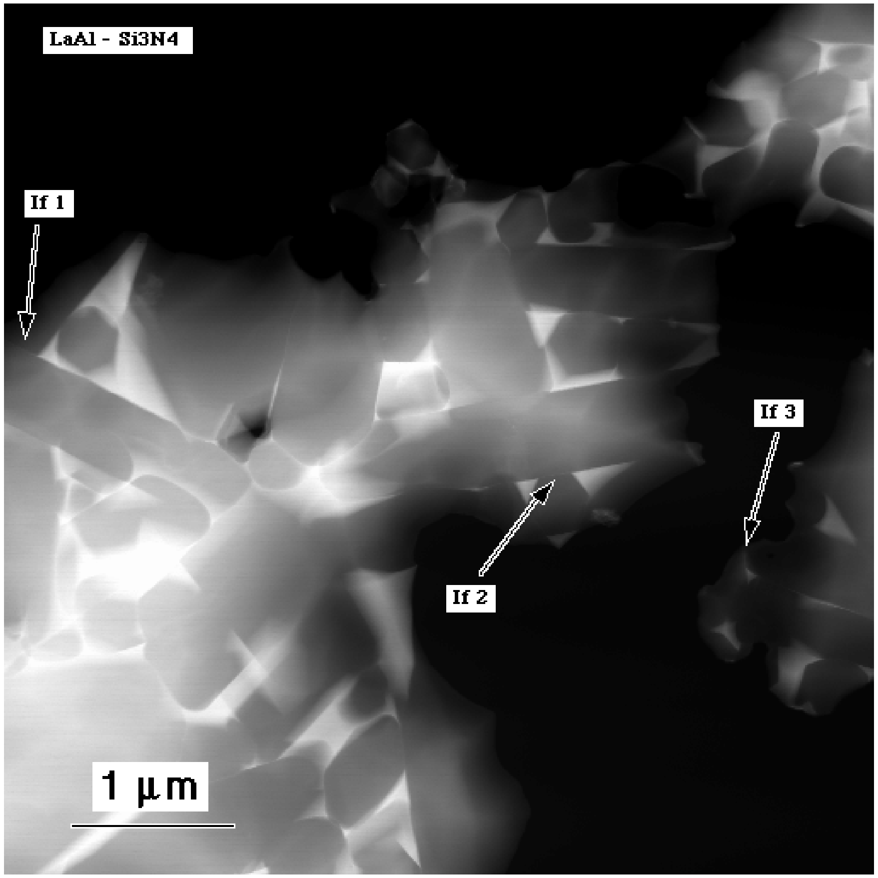
Index of Refraction

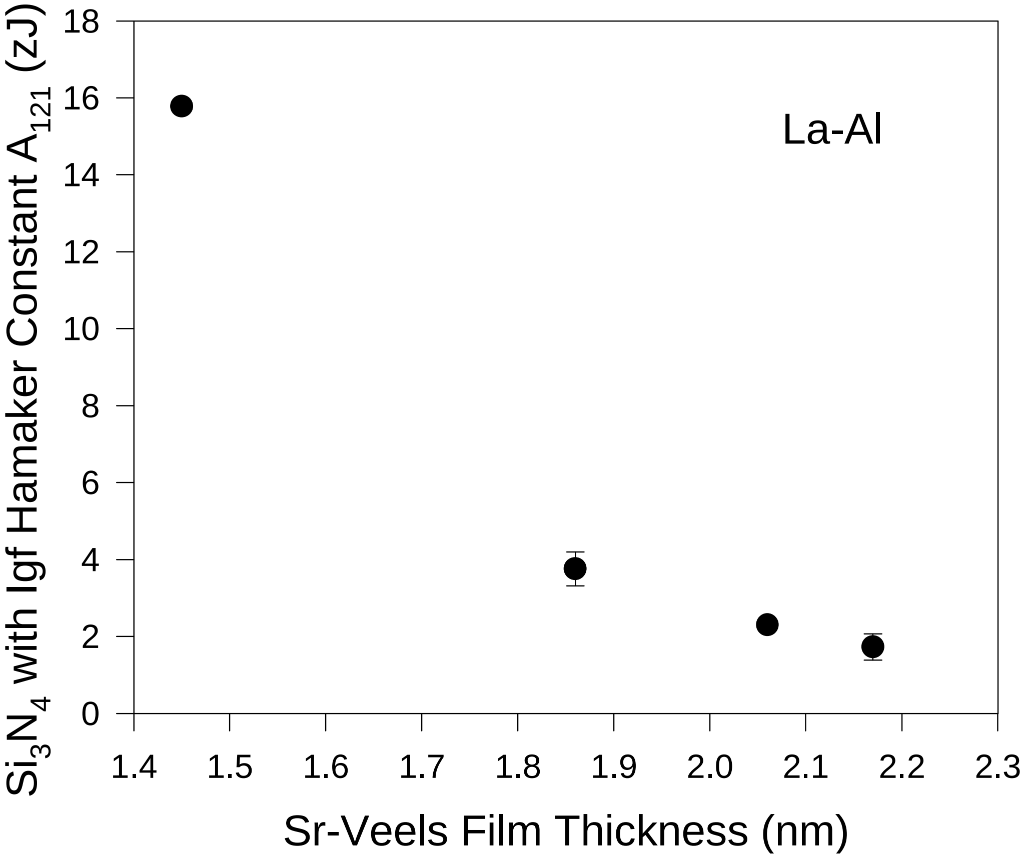
SiON	Mg Glass	Al Glass
Y	1.78 1.71	
Lu	1.70	1.776
La		1.832
Gd		1.826
Si_3N_4 Bulk	1.96	

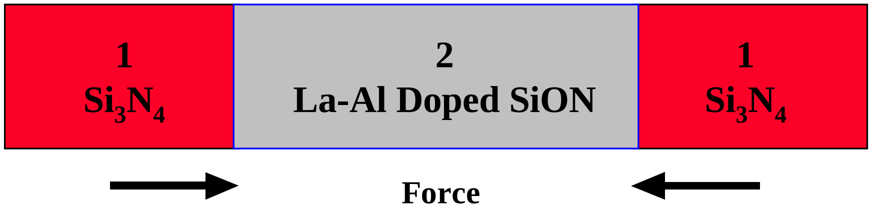
A_{121} Hamaker Constant (zJ)

SiON	Mg Glass	Al Glass
Y	4.54 6.50	
Lu	7.86	5.06
La		2.72
Gd		4.64
Si_3N_4 Bulk	180.8	

IG Film Thickness Vary With Dispersion Force







1 Si_3N_4	2 La-Al Doped SiON	1 Si_3N_4

→ **Force** ←

Thickness of Equilibrium Intergranular Films

- In Silicon Nitride

Vary With Magnitude of the London Dispersion Force at the Interface

R. H. French, H. Müllejans, D. J. Jones, G. Duscher, R. M. Cannon, M. Rühle, **Acta Materialia**, **46**, 7, 2271-87 (1998).

Interfacial Segregation of RE in Si_3N_4

From Periodically Averaged HAADF-STEM Images

RE Segregation To Interface

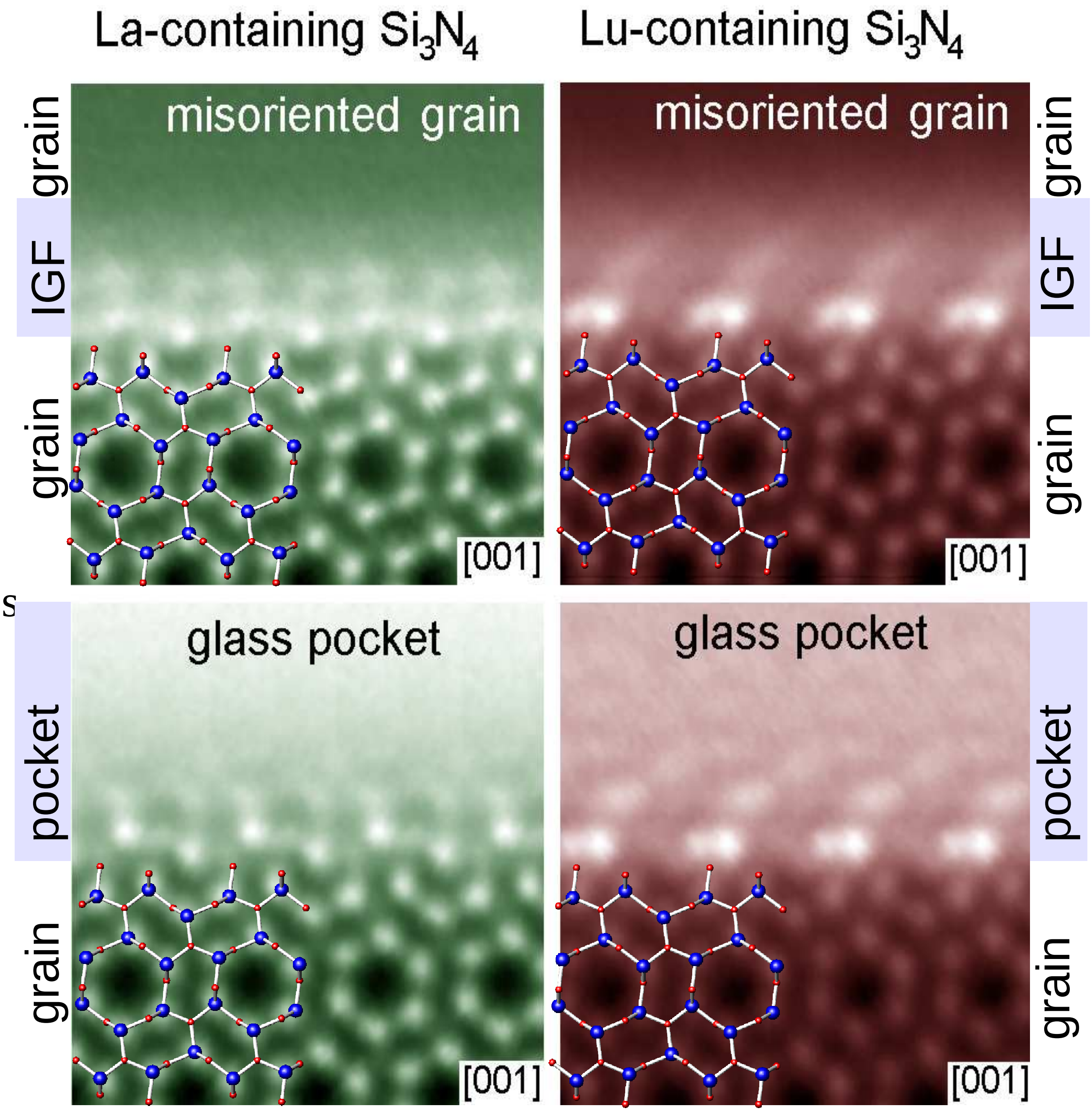
At Grain/Film Interface

And At Grain/Triple Pocket Interfaces

Different Average Atomic Arrangement Of La & Lu

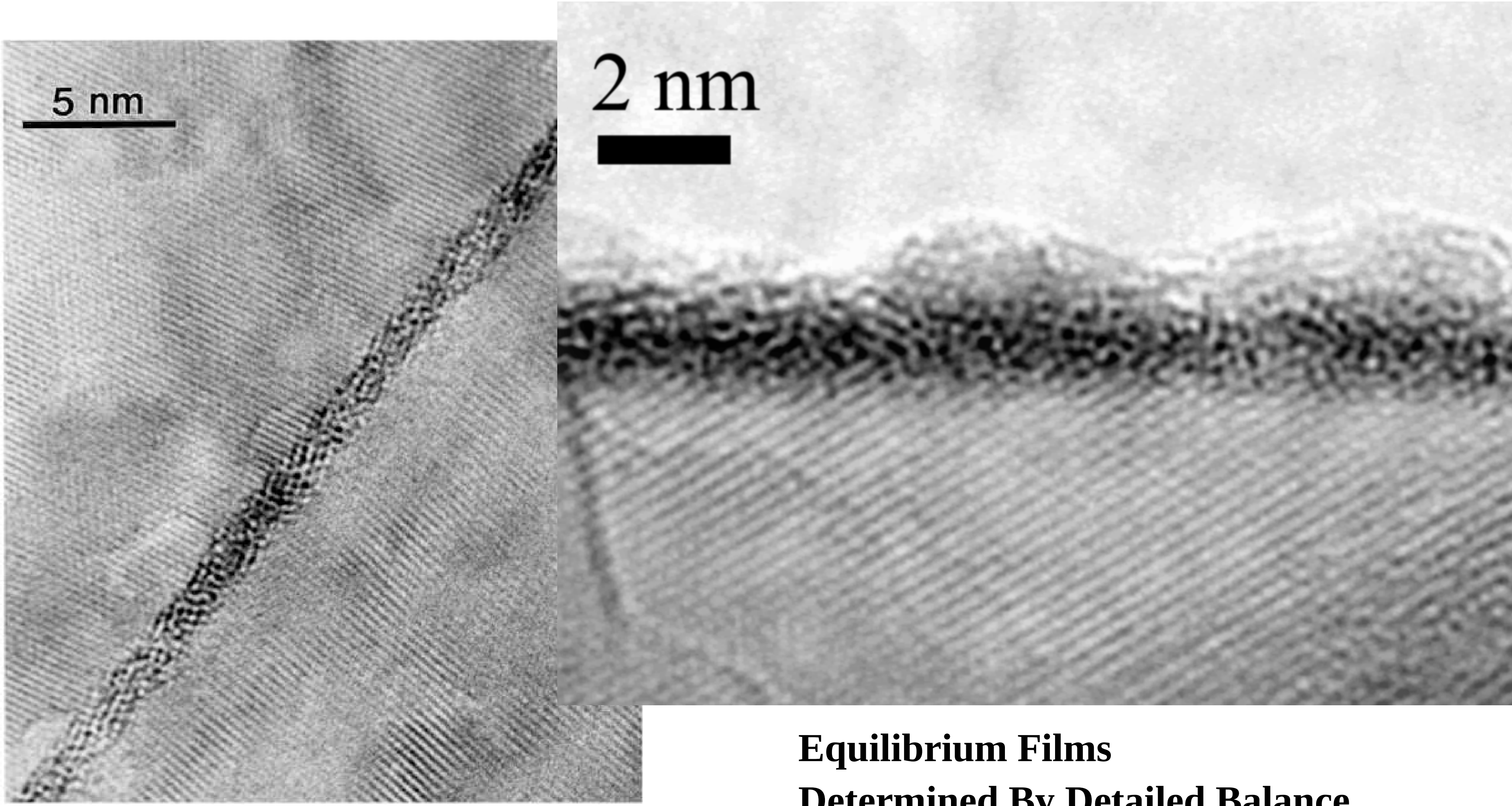
In RE-M-SiON:Si_3N_4

- M = Mg
- RE = La, Lu



G.B. Winkelman, C. Dwyer, D.J.H. Cockayne, 1Department of Materials, University of Oxford

Bi_2O_3-doped ZnO: Interfacial & Surficial Films



Equilibrium Films

Determined By Detailed Balance

- Of Dispersion Forces
- And Other Forces

J. Luo, H. Wang, and Y.-M. Chiang, "Origin of Solid-State Activated Sintering in ZnO-Bi_2O_3," **J. Am. Ceram. Soc.**, **82**[4] 916-20 (1999).

Optical Properties And Electronic Structure

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Bulk: VUV- LPLS Spectrophotometer

Laser Plasma Light Source

- Samarium

Spectral Range

- 1.5 to 44 eV
- 700 to 28 nm

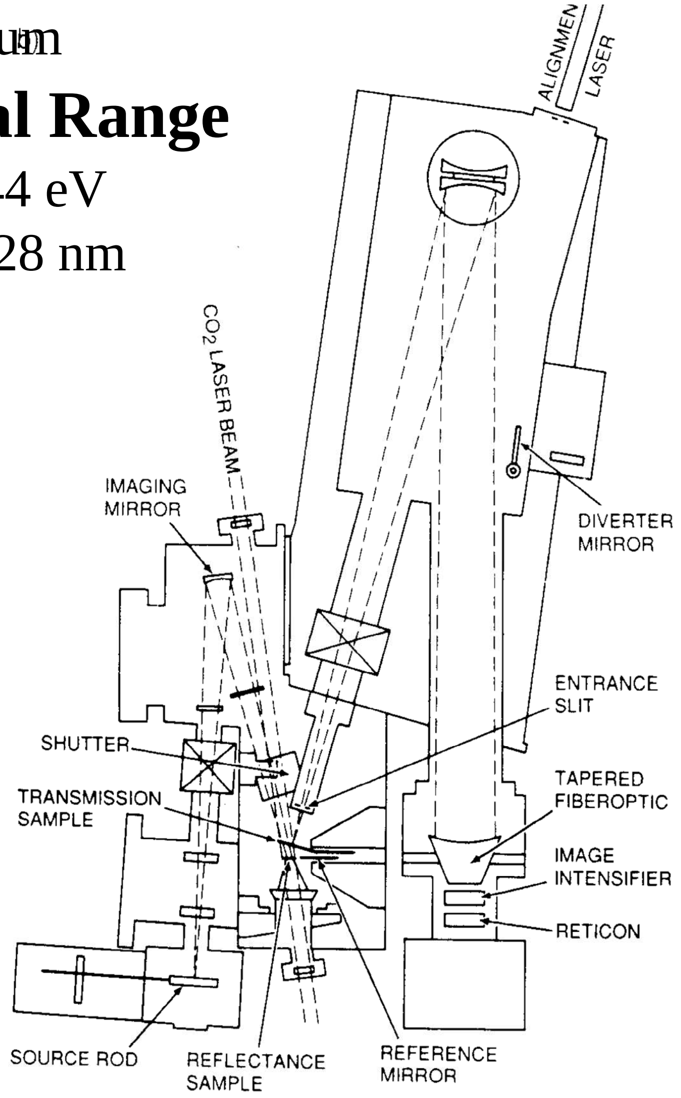
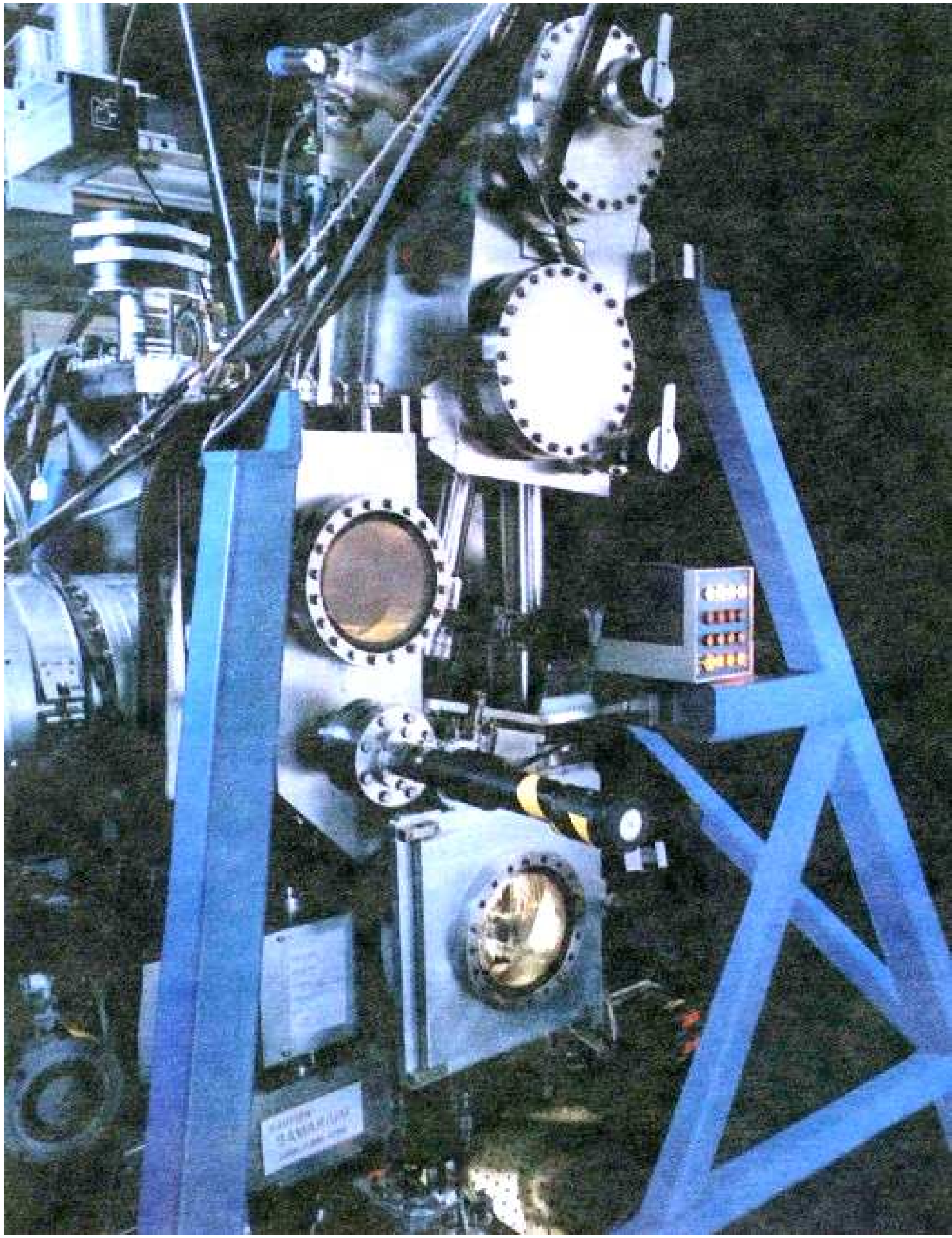


Fig. 1. (q) Block diagram of the major elements of the LPLS spectrophotometer. (b) schematic representations of the LPLS spectrophotometer.



M. L. Bortz, R. H. French, Applied Physics Letters, 55, 19, 1955-7, Nov. 8, (1989).
R. H. French, Physica Scripta, 41, 4, 404-8, (1990).

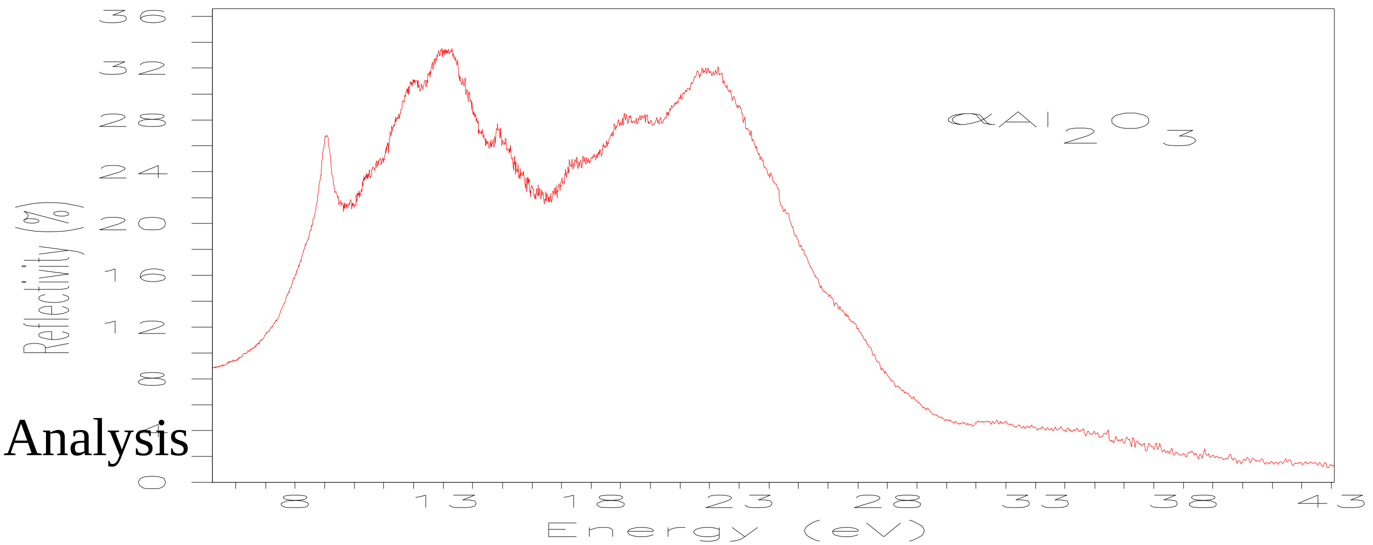
VUV Reflectance and Interband Transitions

VUV Reflectance

- Linear Response Func.

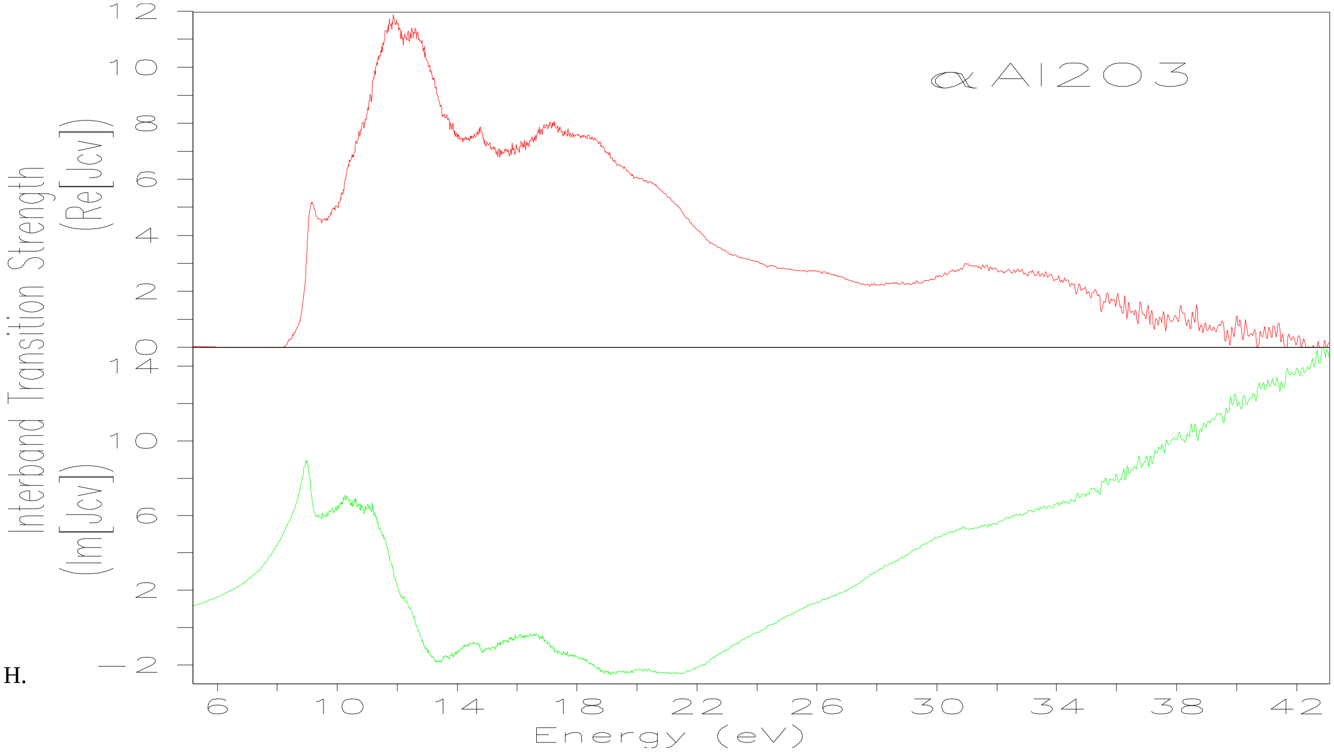
$$\theta(E) = -\frac{2E}{\pi} \mathrm{P}\int_{0}^{\infty} \frac{\ln\{\rho(E')\}}{E'^{2}-E^{2}}\,\mathrm{d}E'$$

Kramers Kronig Dispersion Analysis



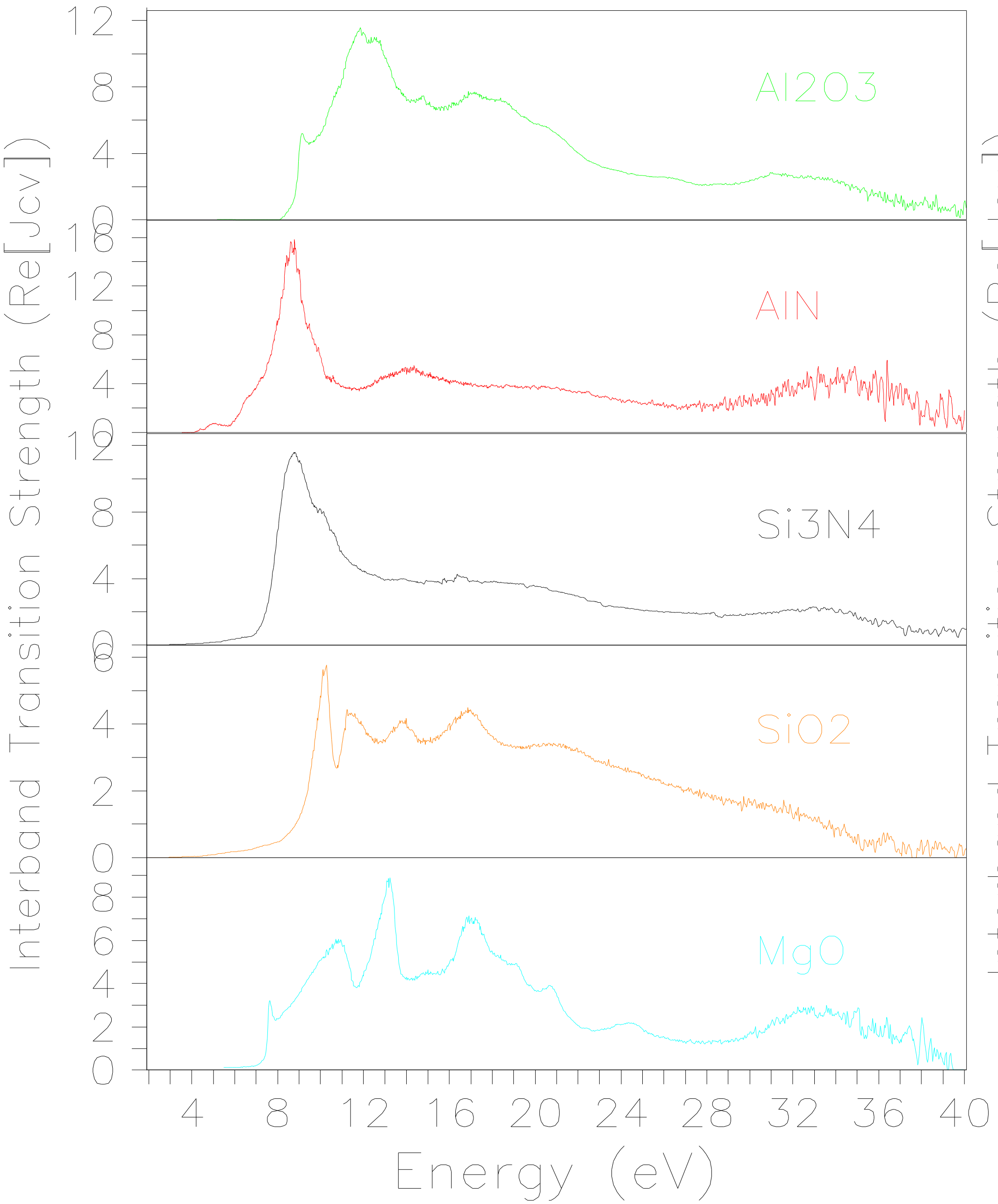
Interband Transition Strength

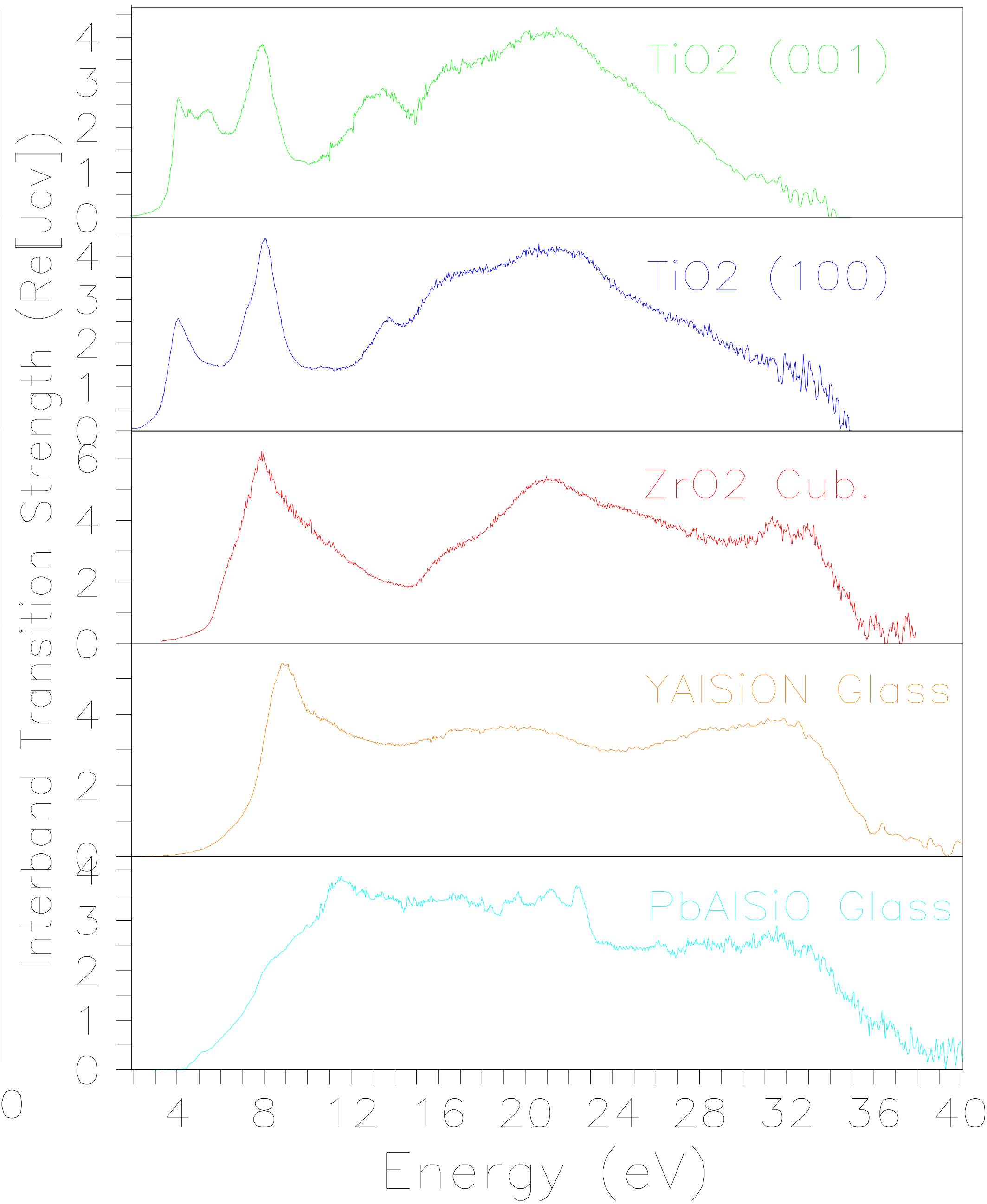
$$J_{cv} = i\frac{E^{2}}{8\pi^{2}}(\varepsilon_{1}+i\varepsilon_{2})^{*}$$



M. L. Bortz, R. H. French, Applied Physics Letters, 55, 19, 1955-7, Nov. 8, (1989). R. H. French, Physica Scripta, 41, 4, 404-8, (1990). M. L. Bortz, R. H. French, , Applied Spectroscopy, 43, 8, 1498-1501, (1989).

Electronic Structure of Ceramics





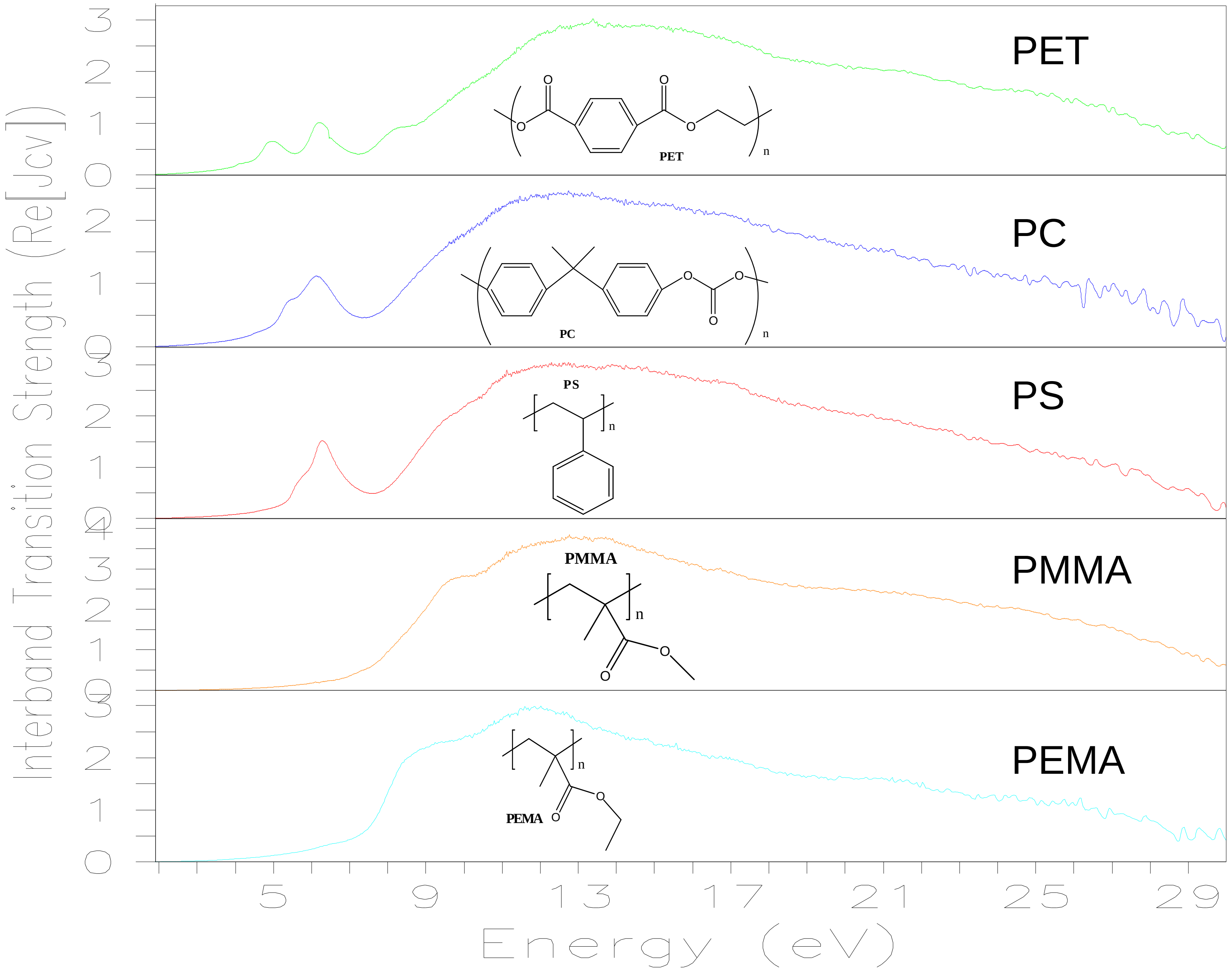
Electronic Structure of Polymers

Hierarchy Of Transitions

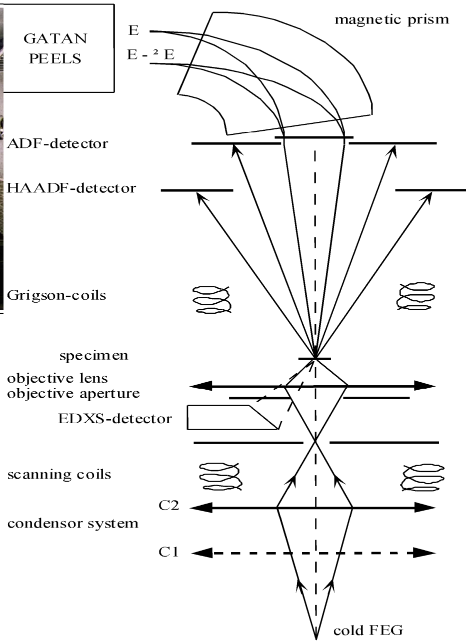
- Aromatic:
  - π→ π*
- Carbonyl:
  - n→ σ* ,
- C-C Backbone:
  - σ→ σ*

Dimensionality Of Transitions

- Critical Points
- Or Spectral Lineshapes



Interfaces: Valence Electron Energy Loss Spectroscopy



Energy Loss Function

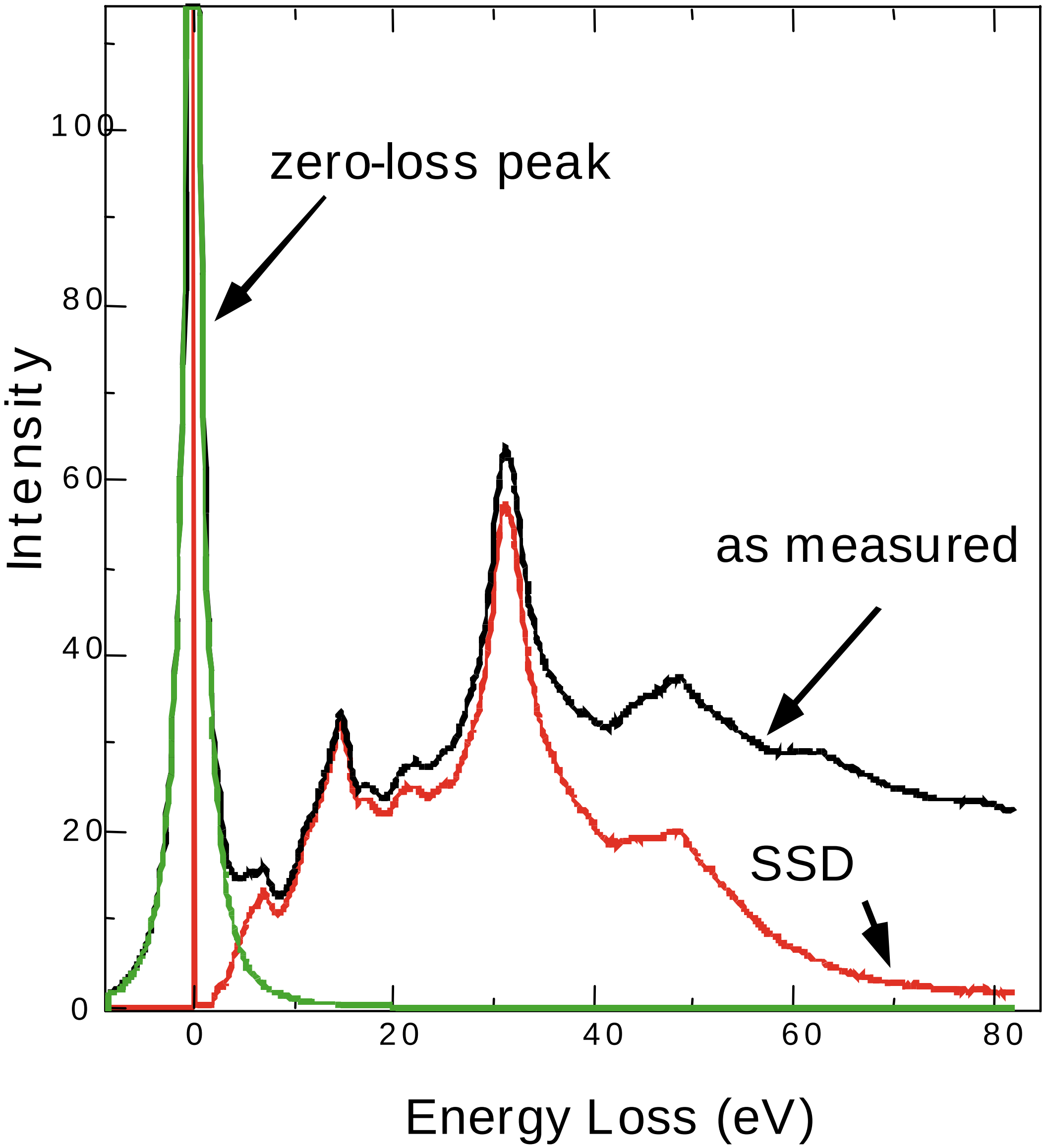
- An Optical Property

Energy Loss Regimes

- Core EELS:
- Near Edge EELS:
- **Valence EELS:**
  - Interband Electronic Structure
  - Too Complex To Analyze?

Scanning Transmission Electron Microscope Spatially Resolved Microscopy

- Probe Size: ~1.0 nm
- Energy Resolution: 0.6 eV
- Linescans (100 Spectra in 40 nm)



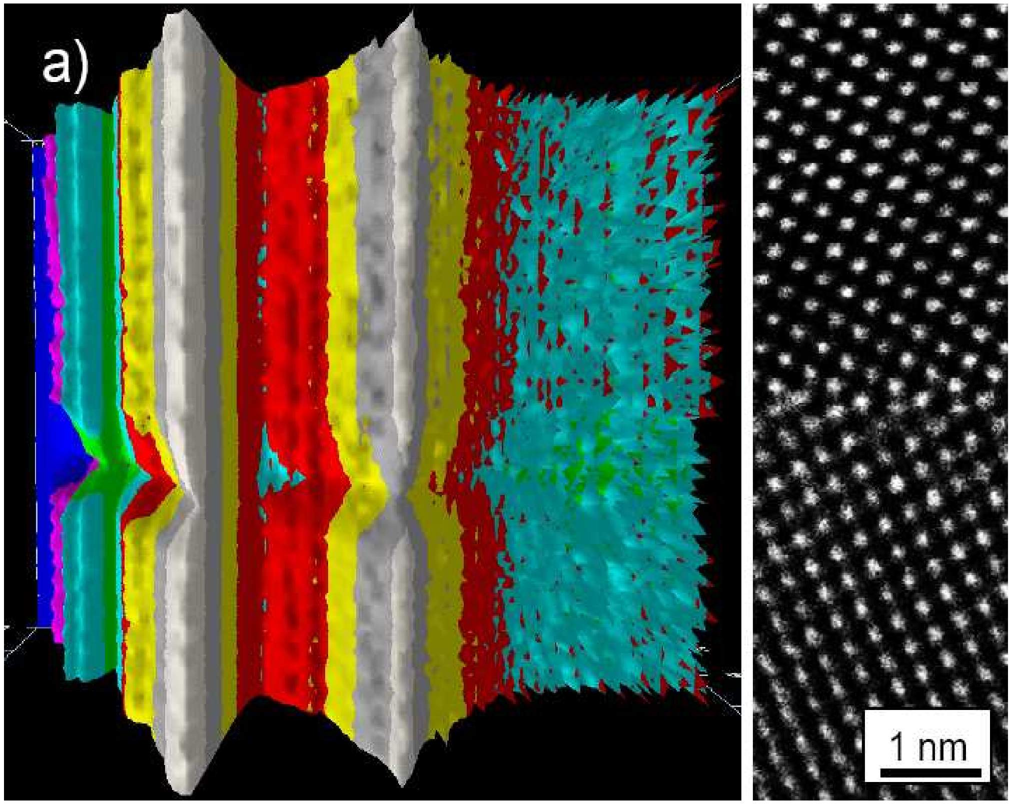
Single Scattering Deconvolution
Kramers Kronig Analysis
London Dispersion Transform

R. H. French, et. al., **Acta Materialia**, **46**, 7, 2271-87, (1998). A. D. Dorneich,et. al., **J. Microscopy**, **191**, 3, 286-96 (1998).

$SrTiO_3$:Fe Bicrystals

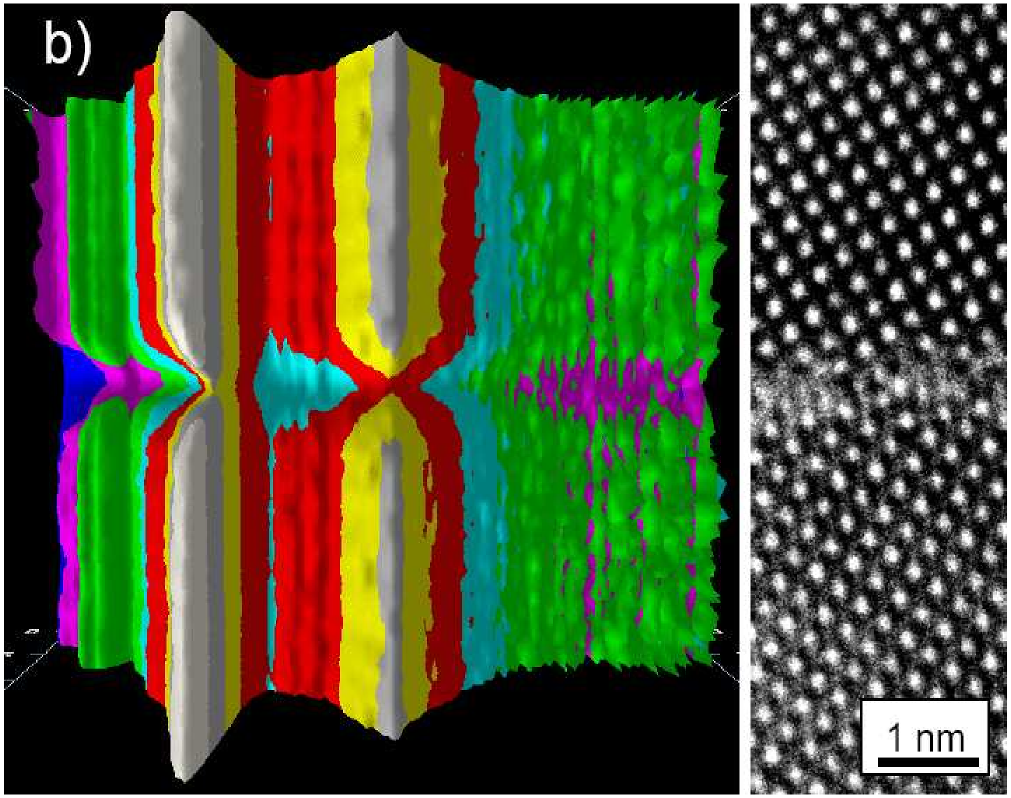
Σ 5 Boundary

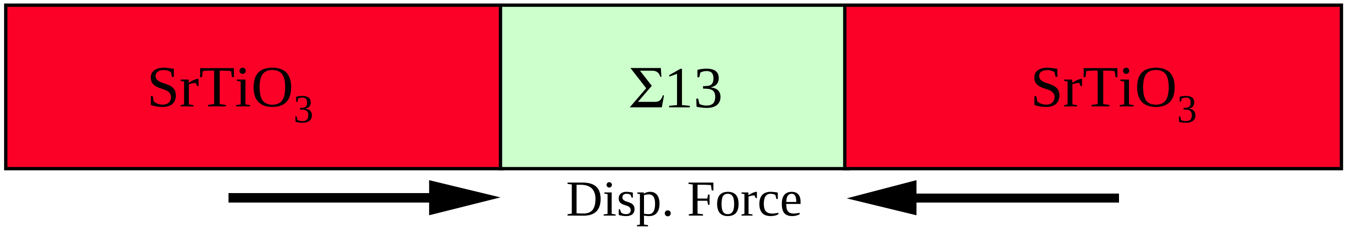
- Atomically Structured



nΣ 13 Boundary

- Atomically Structured





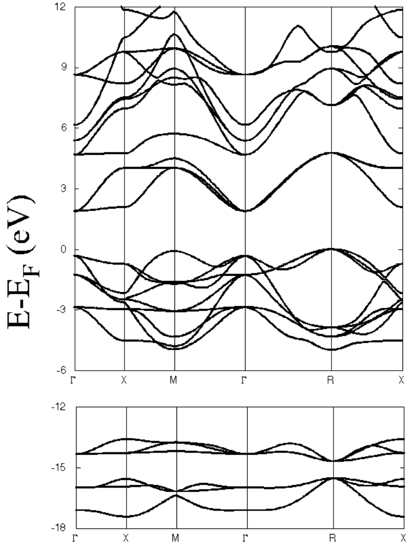
$SrTiO_3$ | Σ13 | $SrTiO_3$

→ Disp. Force ←

K. van Benthem, G. L. Tan, L. K. Denoyer, R. H. French, M. Rühle, **Phys. Rev. Lett.**, **93**, 227201, (2004),
K. van Benthem , G. Tan, R. H. French, L. K. Denoyer, R. Podgornik, V. A. Parsegian, **Phys. Rev. B, 74**, (2006).

$SrTiO_3$ Σ5 & Σ13 Interfacial Electronic Structure

Assignments: LDA Band Structure Calc.

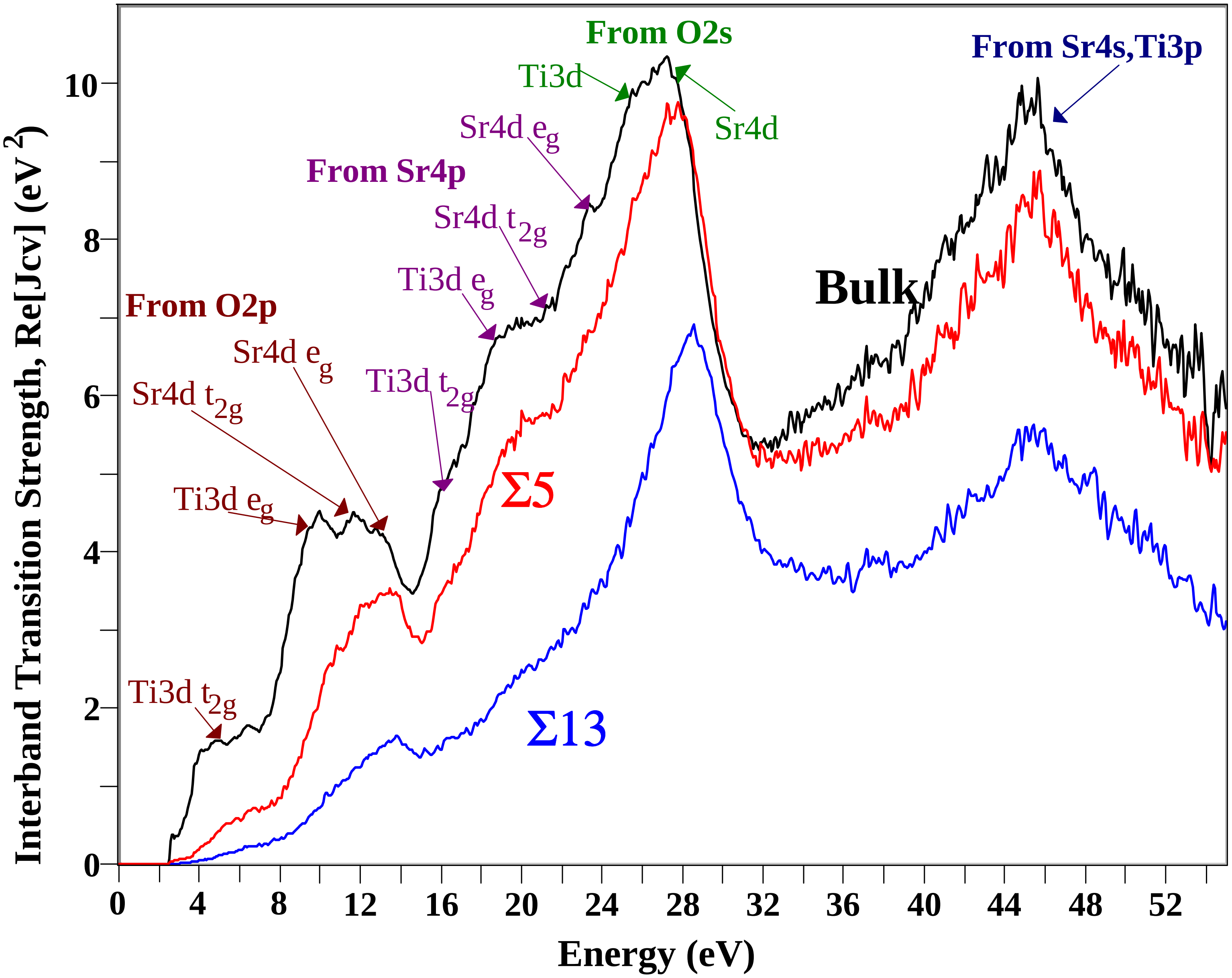


Loss of Transitions
- From O2p
- To Ti3d

Removal of Ti
- In Boundary

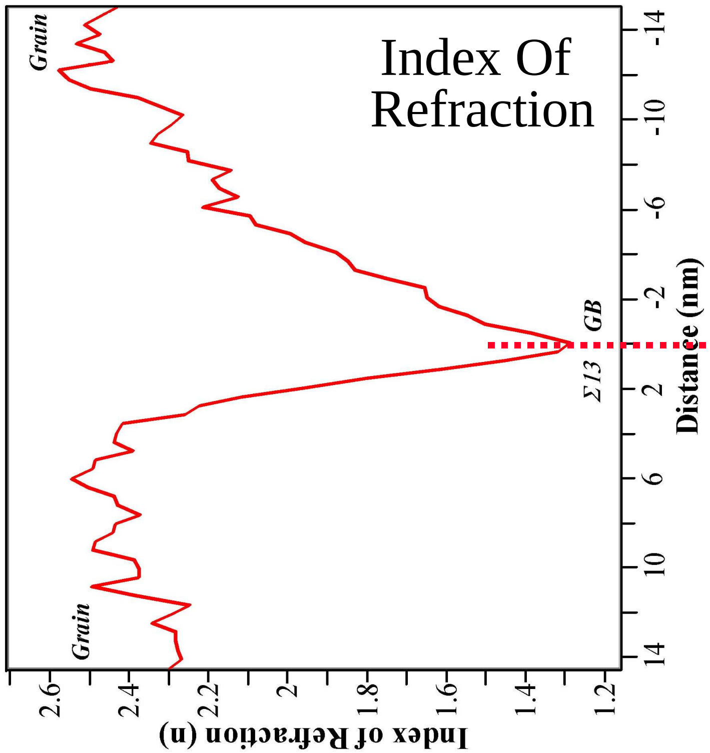
Σ5 GB
- Ti3d t2g Reduced
- Sr Present

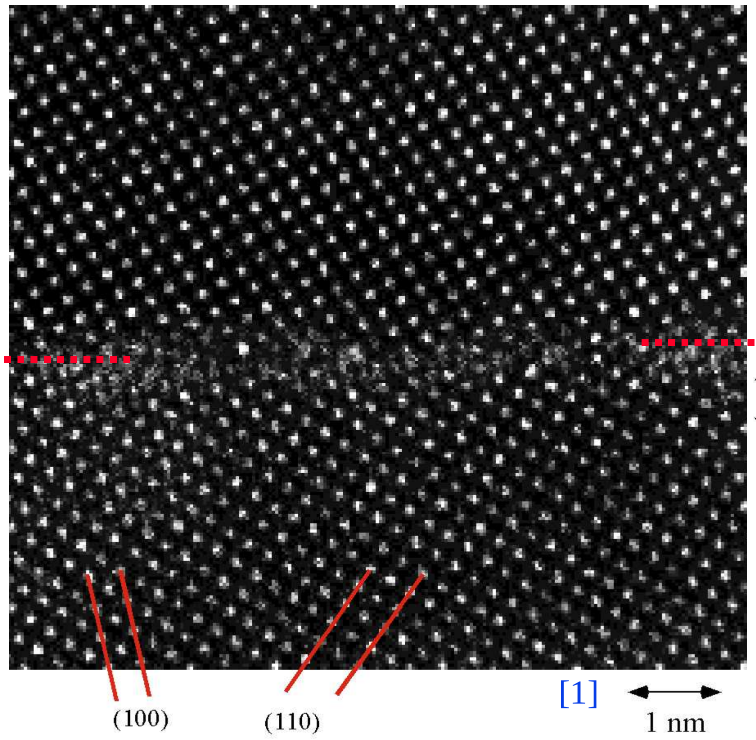
Σ13 GB
- Ti3d t2g Reduced
- Sr Present

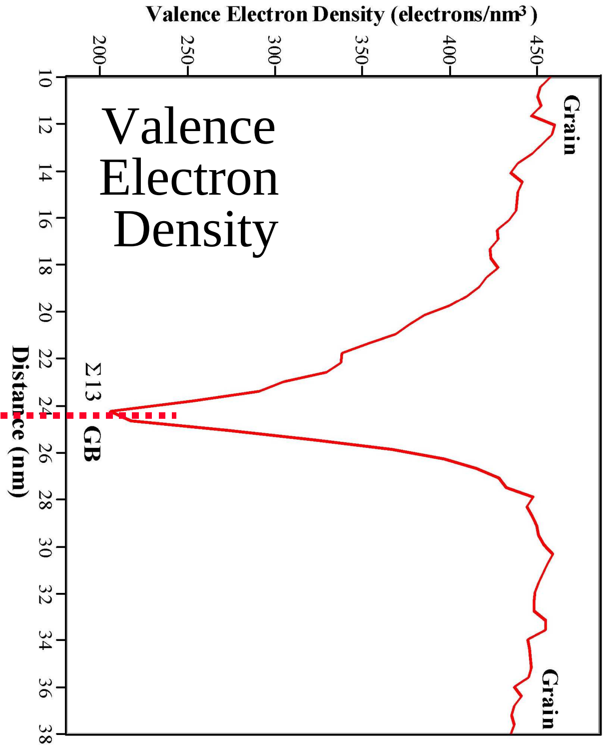


K. van Benthem, C. Elsässer, R. H. French, **J. Appl. Phys.**, **90**, 12, 6156-64, (2001).

Measured Properties Gradients At Grain Bndry





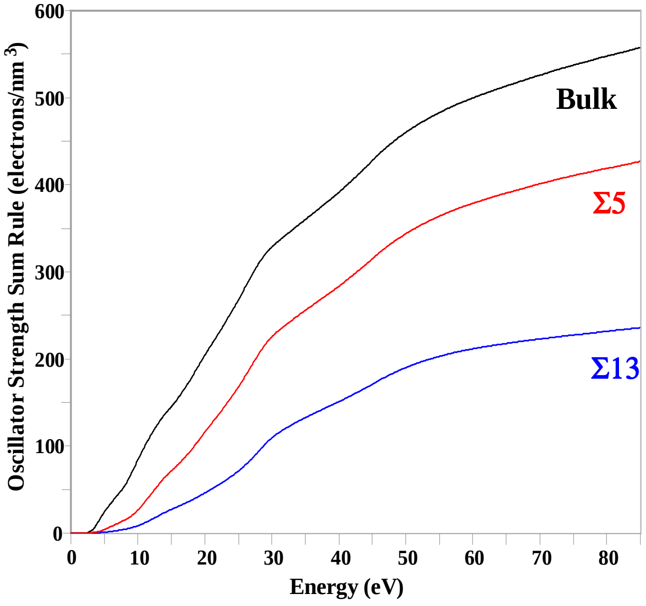


nΣ13 Grain Boundary In $SrTiO_3$

- Valence EELS in STEM

Measure GB Core

- Index Of Refraction
- Electron Density / nm^3



van der Waals – London

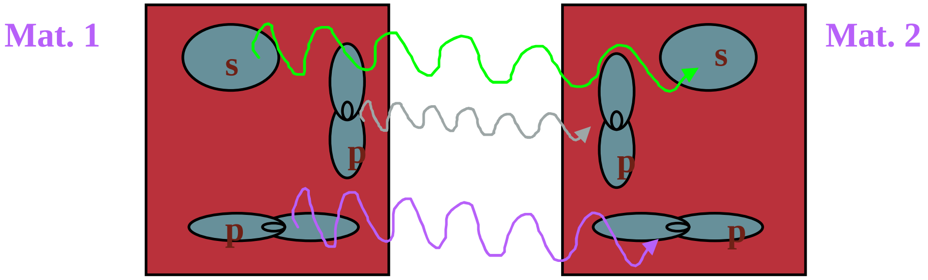
Dispersion Interactions

The miracles of science™

Origin of The London Dispersion Interaction

van der Waals-London Dispersion Interactions

- Thermodynamic Free Energy



Arise From Oscillating Dipoles

- Interatomic Bonds of Elect. Struc.

J_{cv} , ε" => London Disp. Spectra

A - Hamaker Constant

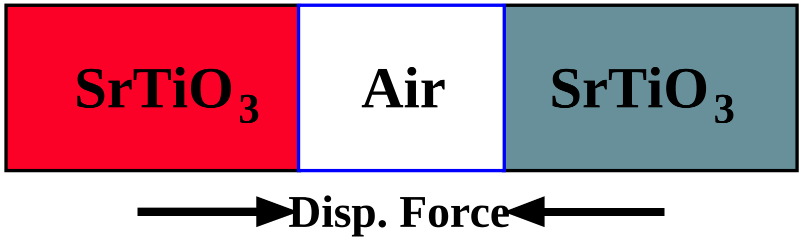
- F_{disp} - Dispersion Force

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

Attractive Force: Nonwetting

- Positive **Hamaker Constant**

A_{123}

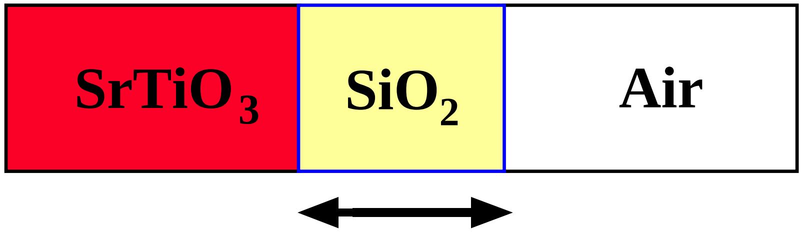


248 zJ

120 zJ

Repulsive Force: Wetting

- Negative **Hamaker Constant**



-68 zJ

Full Spectral Hamaker Constants

Using Lifshitz Theory, QED

- Acquire Exp. Spectra
- Calc. London Disp. Spectrum
  - Kramers Kronig Transform

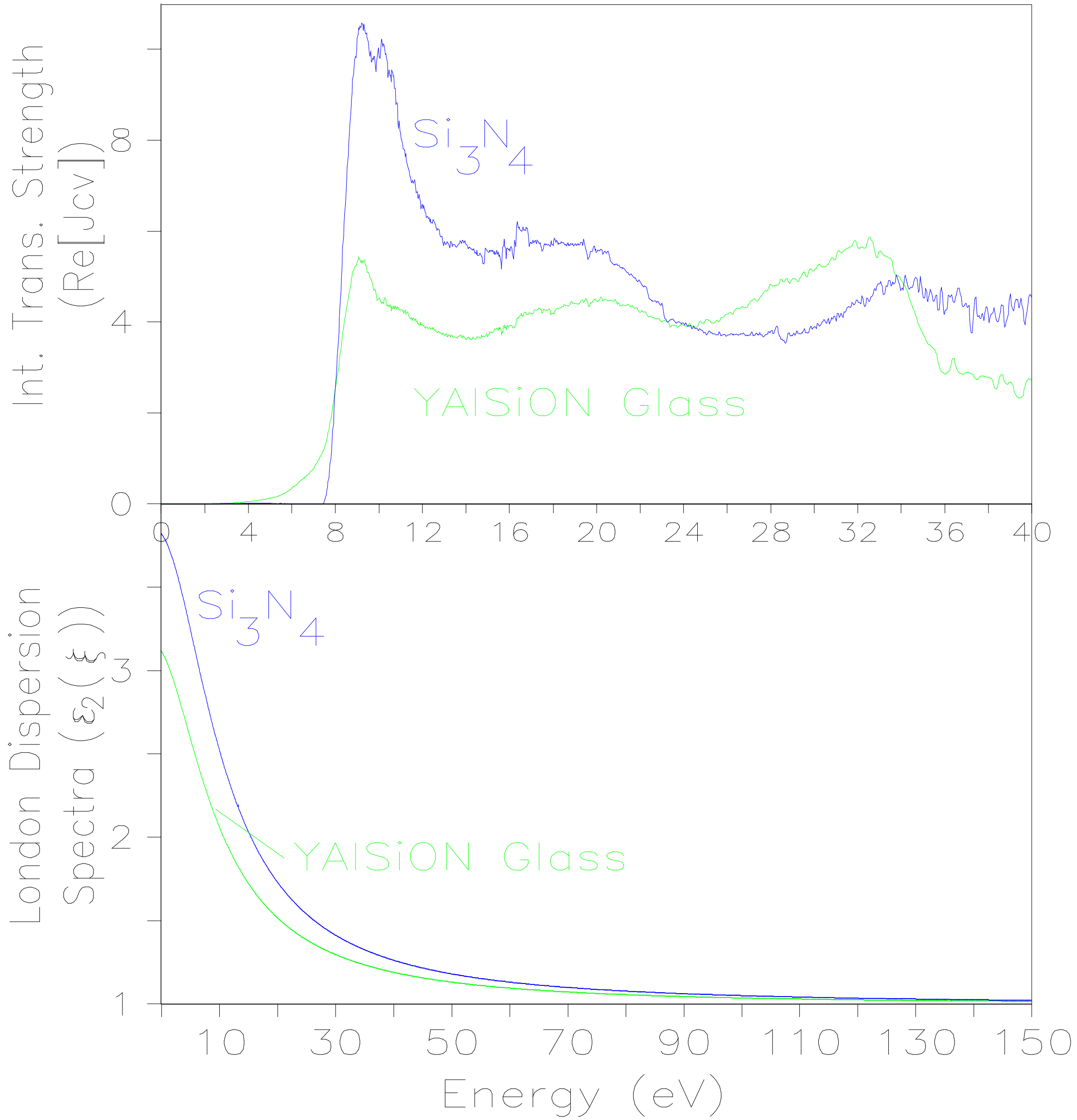
$$\varepsilon_2(\xi)=1+\frac{2}{\pi}\int_0^\infty\frac{\omega\varepsilon_2(\omega)}{\omega^2+\xi^2}d\omega$$

- Then Hamaker Constant
  - Calc'd by Spectral Differences
  - of London Disp. Spectra

$$A=\frac{-3\eta L^2}{\pi}\int_0^\infty\rho d\rho\int_0^\infty\ln G(\xi)d\xi$$

$$G_{121}^{NR}(\xi)=1-\Delta_{12}^2e^{-2a\rho}$$

$$\Delta_{kj}=\frac{\varepsilon_{2,k}(\xi)-\varepsilon_{2,j}(\xi)}{\varepsilon_{2,k}(\xi)+\varepsilon_{2,j}(\xi)}$$



$A(Si_3N_4 | Vac.| Si_3N_4) = 192$ zJ

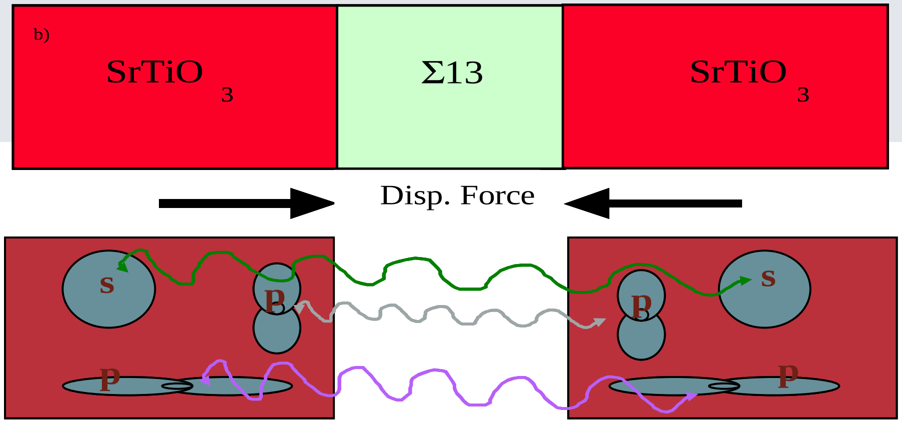
$A(Si_3N_4|YAlSiON|Si_3N_4) = 9.3$ zJ

zJ = 10^{-21} Joules

R. H. French, R.. M. Cannon, L. K. DeNoyer, Y.-M. Chiang, **Sol. State Ionics**, **75**, 13-33, (1995).

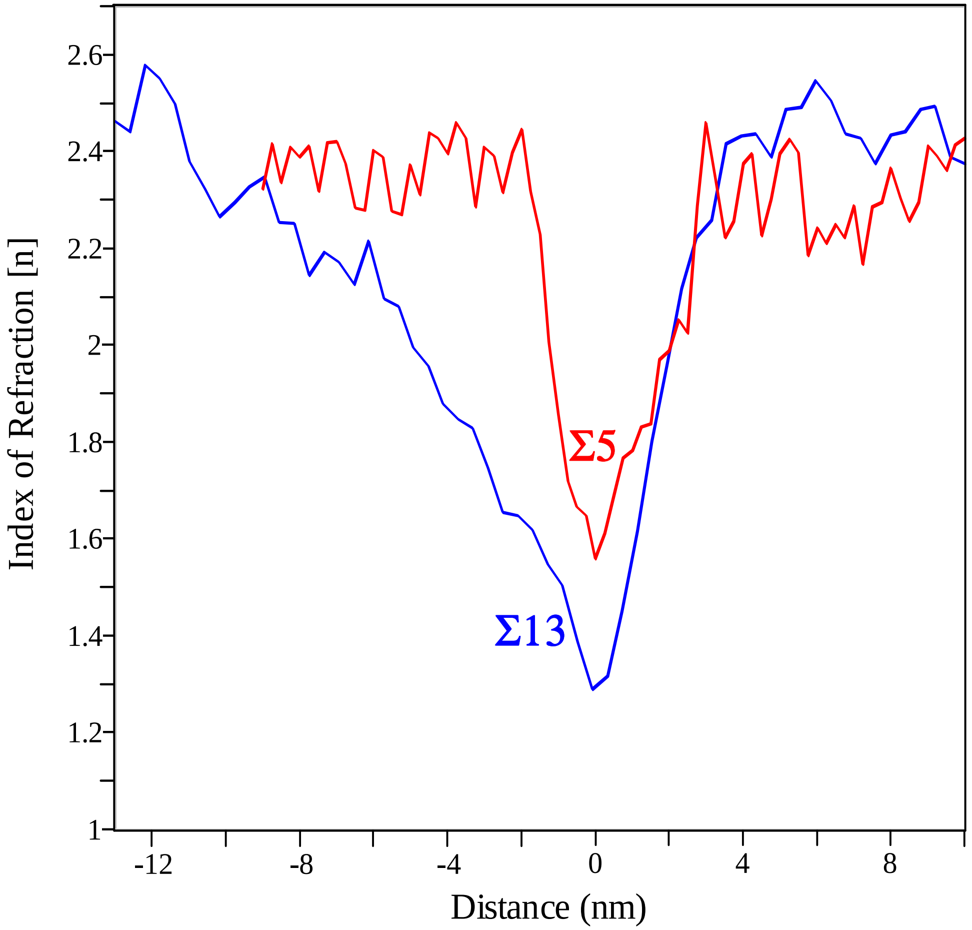
vdW-Ld Energies
of
Grain Boundaries

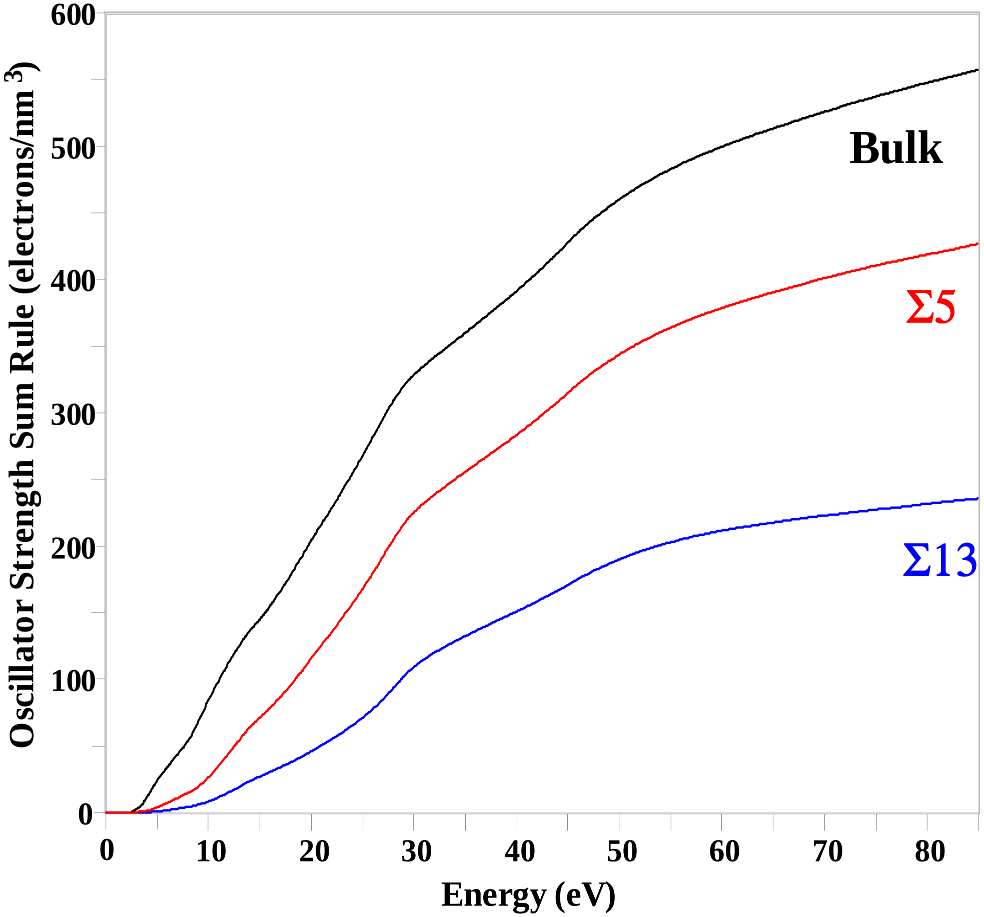
Atomically Structured
Σ5 and nΣ13 $SrTiO_3$ Grain Boundaries



K. van Benthem, G. L. Tan, L. K. Denoyer, R. H. French, M. Rühle, **Phys. Rev. Lett.**, **93**, 227201, (2004),
K. van Benthem , G. Tan, R. H. French, L. K. Denoyer, R. Podgornik, V. A. Parsegian, **Phys. Rev. B, 74**, (2006).

Gradient Properties in Grain Boundaries of $SrTiO_3$





Index of Refraction

- Σ5 Grain Boundary = 1.56
- nΣ13 Grain Boundary = 1.29

n=2.37 for bulk $SrTiO_3$,

- Spectroscopic Ellipsometry.[22]

Valence Electron Density Variations

- From Oscillator Strength Sum Rule

Units of Electrons Per nm^3

- for bulk $SrTiO_3$ Σ5 and nΣ13 GB

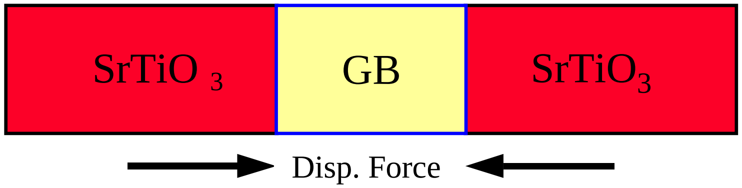
K. van Benthem, C. Elsässer, R. H. French, **J. Appl. Phys**, **90**, 12, 6156-64, (2001), K. van Benthem, et al., **Phys. Rev. Lett., 93**, 227201, (2004), K. van Benthem, et al., **Phys. Rev. B, 74,** 205110, (2006).

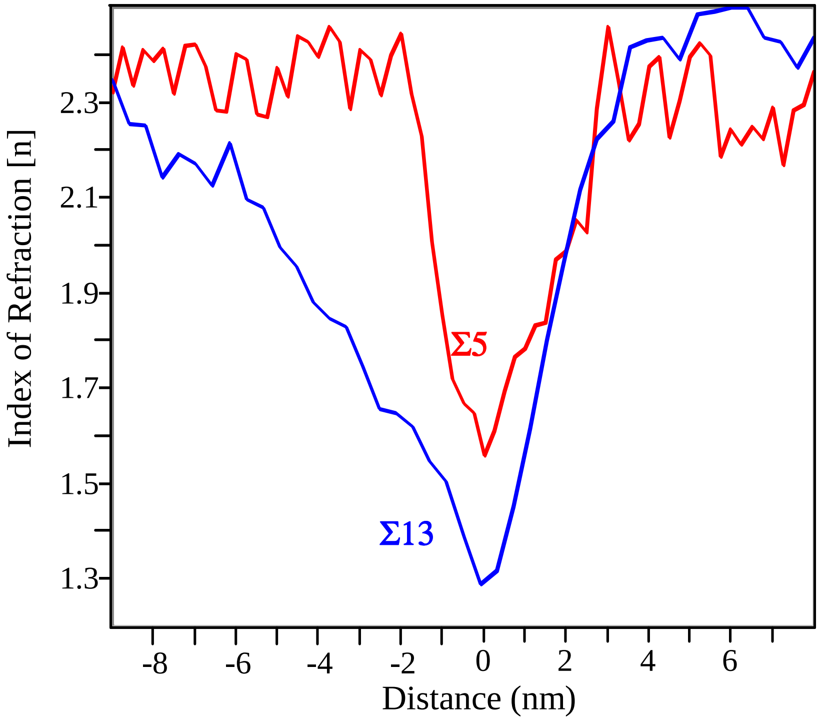
Grain Boundary Dispersion Interaction: A_{121}

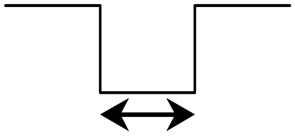
A_{121} Hamaker Constants

- With Sharp Interfaces

Use Of “Bulk” Hamaker?





Interface	Abrupt Gradient  A_{121}^{NR} (zJ)
$SrTiO_3$ | vac. | $SrTiO_3$ d_o=0.195 nm	243.9
$SrTiO_3$ | nΣ13 | $SrTiO_3$ d_o=0.195 nm	105.5
$SrTiO_3$ | Σ5 | $SrTiO_3$ d_o=0.195 nm	35.0
SiO_2 | vac. | SiO_2 d_o=0.165 nm	68.2

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

Σ13 Grain Boundary: Larger Disp. Int.

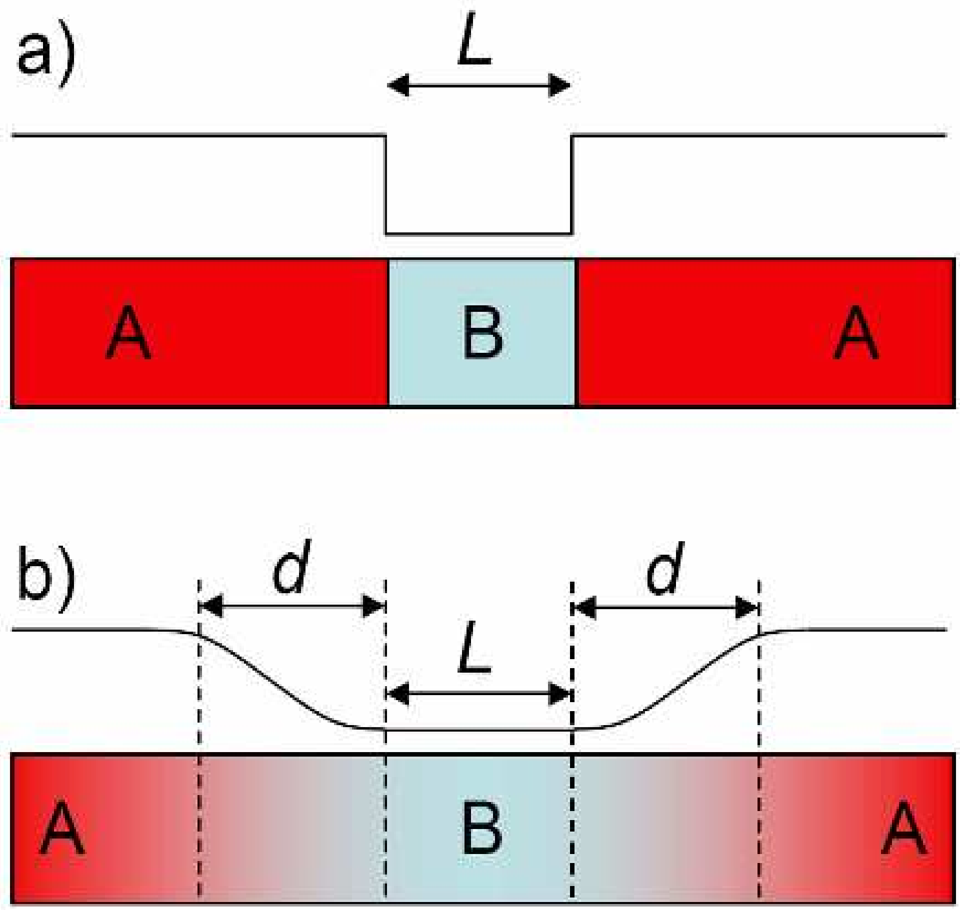
- Than A ($SrTiO_3$ | Silica | $SrTiO_3$) = 71 zJ
- Than A (SiO_2 | Vacuum | SiO_2) = 68.2 zJ

Σ5 Grain Boundary: Larger Disp. Int

- Than Most Intergranular Films

K. van Benthem , G. Tan, R. H. French, L. K. Denoyer, R. Podgornik, V. A. Parsegian, **Phys. Rev. B, 74**, (2006).

A Graded Interface Approach



The Sharp Interfaces of a 1|2|1 Type Model

- Have Unrealistic Infinite Property Gradients

Are These Sharp Interface Results

- Applicable To Grain Boundaries?

Nanoscale Approach To Apply

- Bulk Continuum Dispersion Theory

Use Graded Interface Model

- Interfaces With Finite Property Gradients
  - [1 | gradient | 2 | gradient | 1]

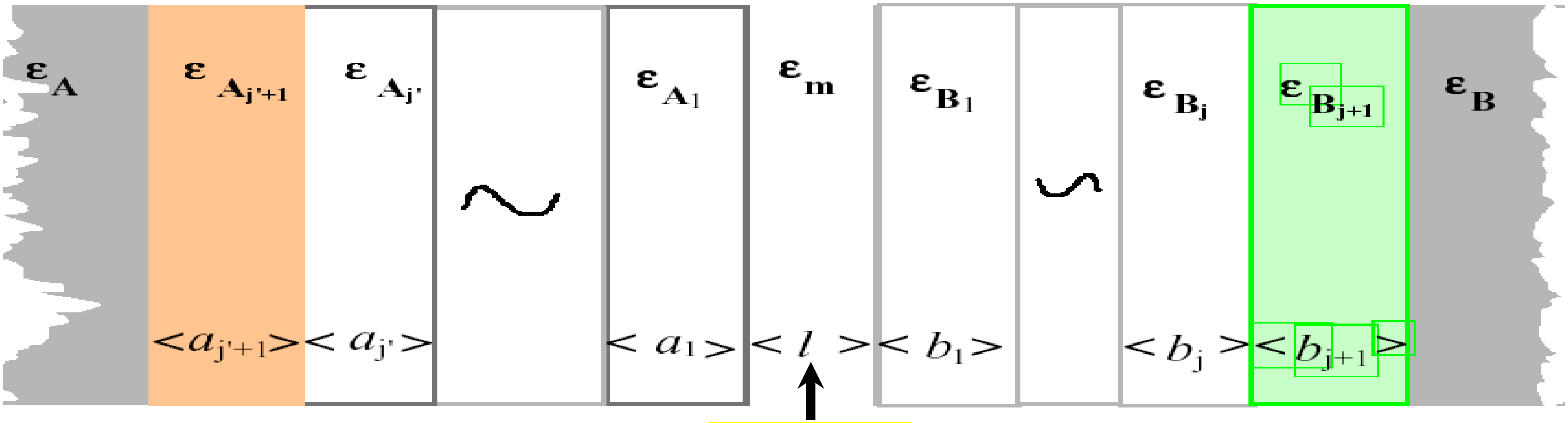
Define Finest Length Scale For Gradients

- Use A Characteristic Interatomic Bond Length
  - For $SrTiO_3$ Use $d_o = 0.19525$
  - The Ti-O Bond Length in $SrTiO_3$

Finest Scale Property Gradients Are Interatomic

K. van Benthem , G. Tan, R. H. French, L. K. Denoyer, R. Podgornik, V. A. Parsegian, **Phys. Rev. B**, 74, (2006).
R. Podgornik, R. H. French, V.A. Parsegian, **J. Chem. Phys.**, 124, 044709, (2006)

Hamaker Coefficients For Arbitrary Multilayers



“Left Side”

Central Layer

“Right Side”

Previously Only 3 or 5 Layer Hamaker Coefficients Tractable

“Add A Layer" Approach

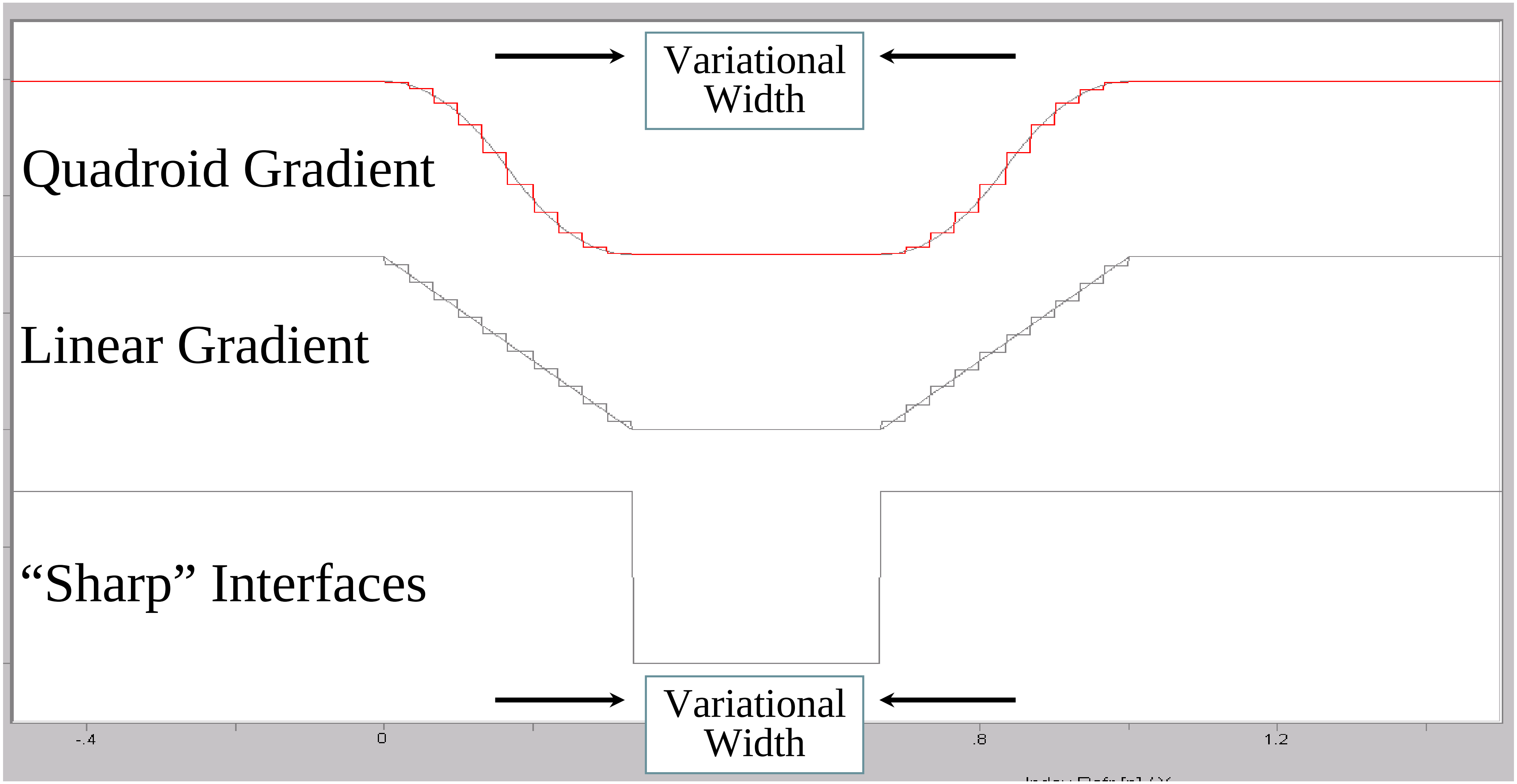
- Matrix Expansion Approach Of Left And Right Half Spaces
- Calculate Effective London Dispersion Spectra
  - For Left and Right Side Of Multilayer Stacks

Fully Retarded Calculations

- Any # of Layers, With A “Central” Layer

R. Podgornik, R. H. French, V.A. Parsegian, **J. Chem. Phys.**, 124, 044709, (2006)

Add-A-Layer Method For Quadroid Gradients



vdW-L Dispersion Energies Of GBs

GB Stabilization Energy

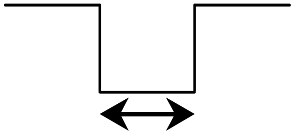
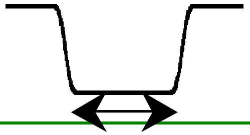
- Due To Dispersion

Abrupt Model Results

- ΔE (nΣ13) = 169 – 73 = 96 mJ/m^2
- ΔE (nΣ5) = 169 – 24 = 145 mJ/m^2

Quadroid Graded Interface Model

- ΔE (nΣ5) = 119 – 14 = 69 mJ/m^2
- ΔE (nΣ13) = 119 – 50 = 105 mJ/m^2

Interface	Abrupt Gradient 		Double-Quadratic Gradient[a] 	
	A_{121}^{NR} (zJ)	E_{London} (mJ.m^{-2})	A_{121}^{R} (zJ)	E_{London} (mJ.m^{-2})
$SrTiO_3$ | vac. | $SrTiO_3$ d_o=0.195 nm	243.9	169	171.2 (L=0.9 nm)	119
$SrTiO_3$ | nΣ13 | $SrTiO_3$ d_o=0.195 nm	105.5	73	72.5 (L=0.9 nm)	50
$SrTiO_3$ | Σ5 | $SrTiO_3$ d_o=0.195 nm	35.0	24	20.7 (L=0.6 nm)	14
SiO_2 | vac. | SiO_2 d_o=0.165 nm	68.2	66	50.3	49

London Dispersion Stabilization Energies For These Atomically Abrupt Grain Boundaries Are Appreciable

Compare To Chemical Energies

- Σ3 GB = 520 mJ/m^2
- Surface Energy ~ 1100/mJ/m^2

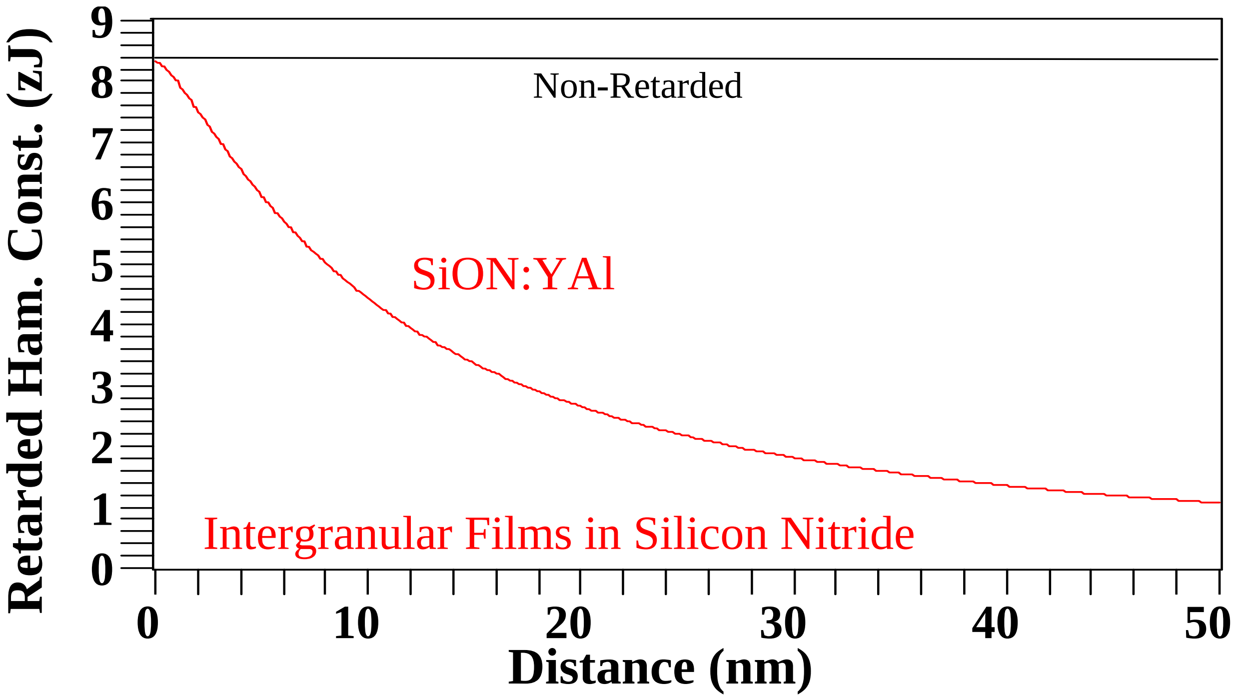
The Role Of Retardation Of vdW-Ld Interactions In Novel Wetting Phenomena

The miracles of science™

Retarded Hamaker Coefficients

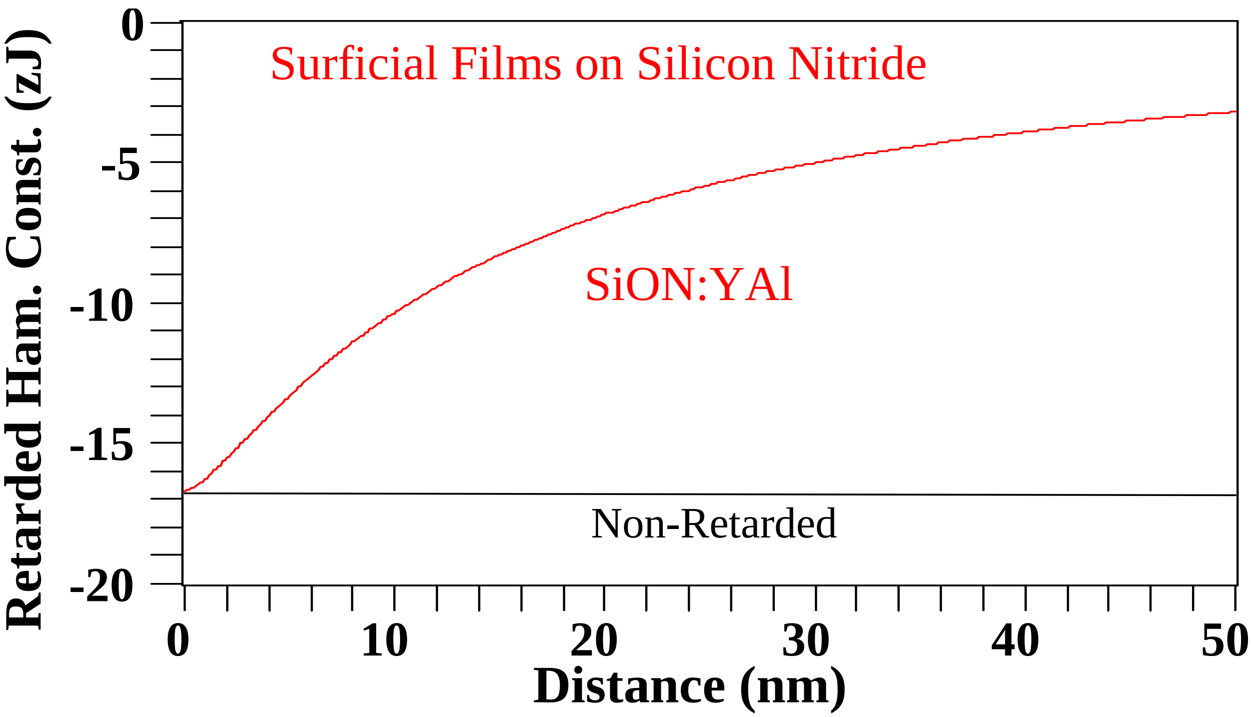
Nonwetting

- Attractive Dispersion Force



Wetting

- Repulsive Dispersion Force



Retardation Length

- Can Exceed 300 nm
- Depending On Details Of System

Equilibrium Surficial Films Of Water On Ice

Retardation of the London Dispersion Interaction

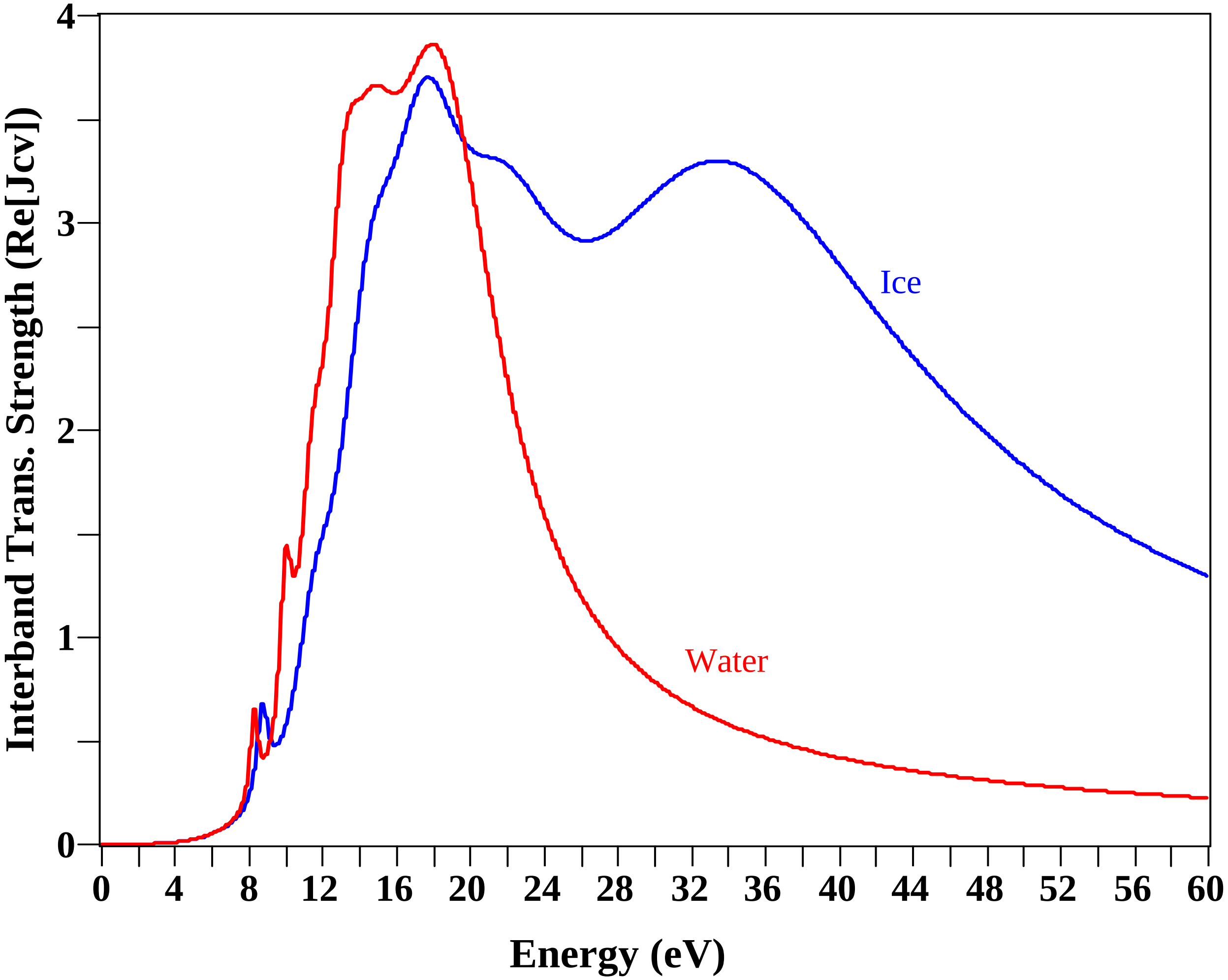
- Leads to Formation Of Surficial Films Of Water On Ice[1]
- Surface Premelting

Equilibrium ~3 nm Water Film On Ice

- Persists to -40°C

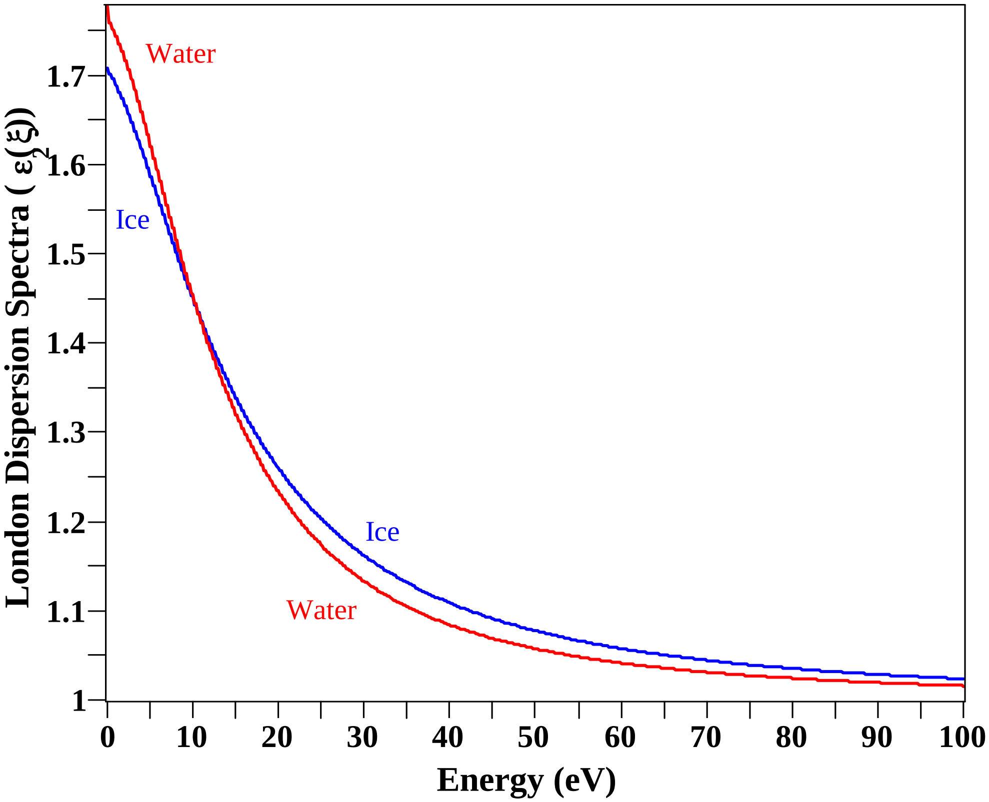
Interband Transitions

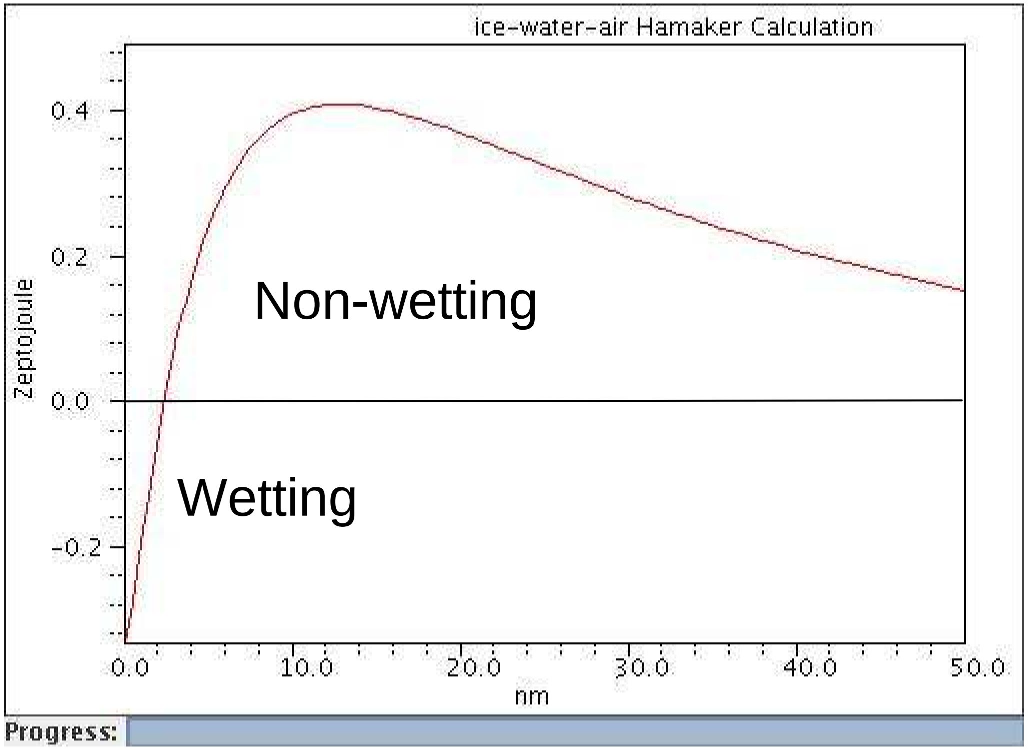
- n(Water) = 1.33
- n(Ice) = 1.31



[1] M. Elbaum, M. Schick, **Phys. Rev. Lett**, 66, 13, (1991); L. A. Wilen, J. S. Wettlaufer, M. Elbaum, M. Schick, **Phys. Rev. B**, 12426.

Equilibrium Surficial Film: Water on Ice





Equilibrium Surficial Film[1]

- Stabilized by Retardation of Dispersion Interaction
- Important To
  - Friction Of Ice
  - Charge Transfer In Clouds

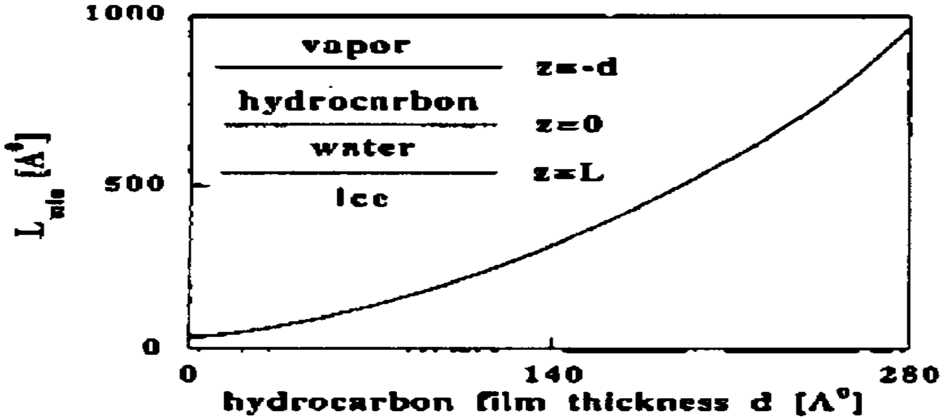
Wetting to Nonwetting Transition

- Multilayer Adsorbate of Water

Addition of Hydrocarbon Surfactant[2]

- For Water on Ice

Water Thickness Increases To 100 nm

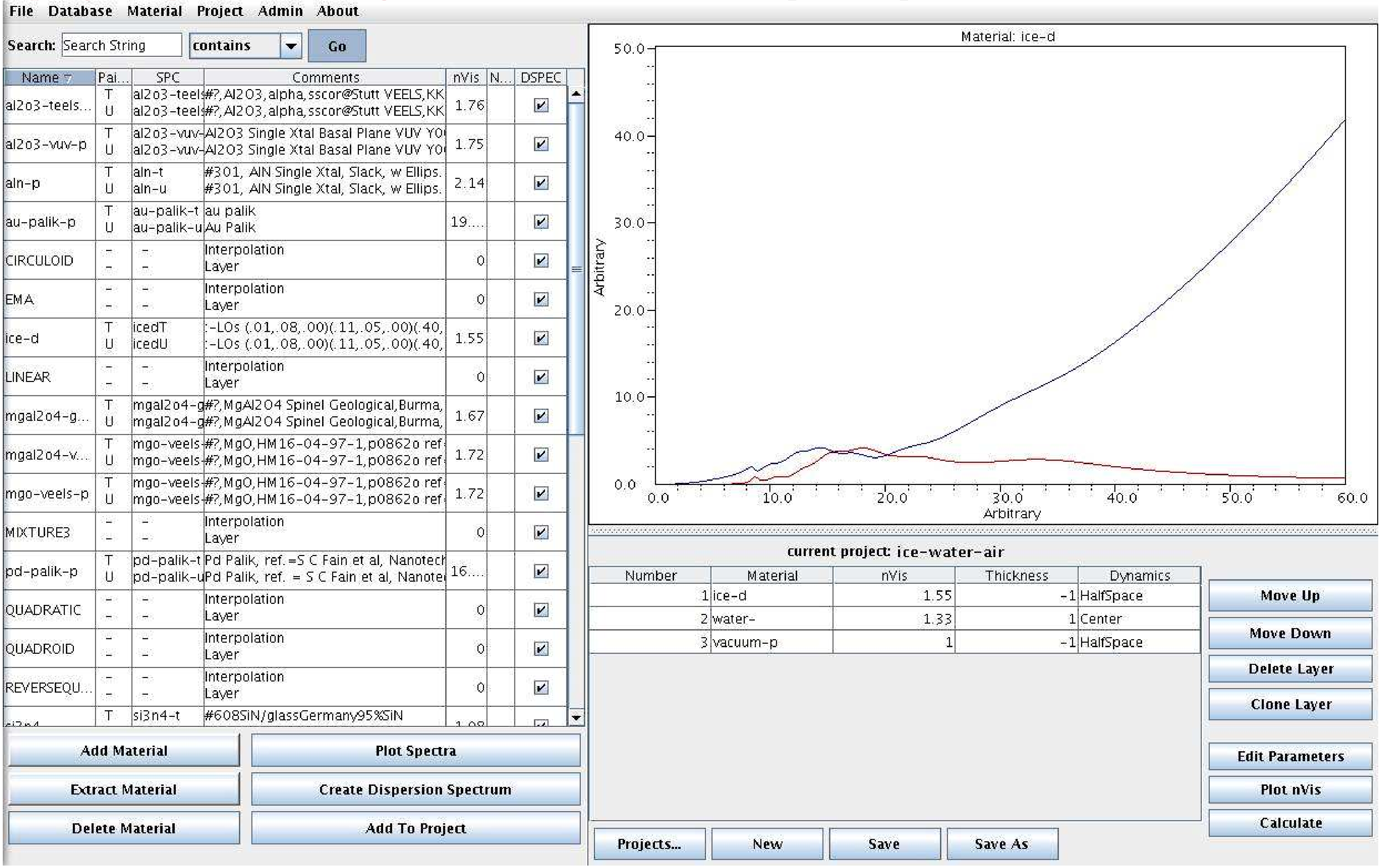


1. M. Elbaum, M. Schick, **PRL**, 66, 13, (1991).
2. R. Bar-Ziv, S. A. Safran, **Langmuir**, 9, (1993).

Gecko Hamaker: Open Source Hamaker Program

Full Spectral, Retarded Hamaker, Coefficients:

http://geckoproj.sourceforge.net/ Distributed With Optical Spectra Of Materials

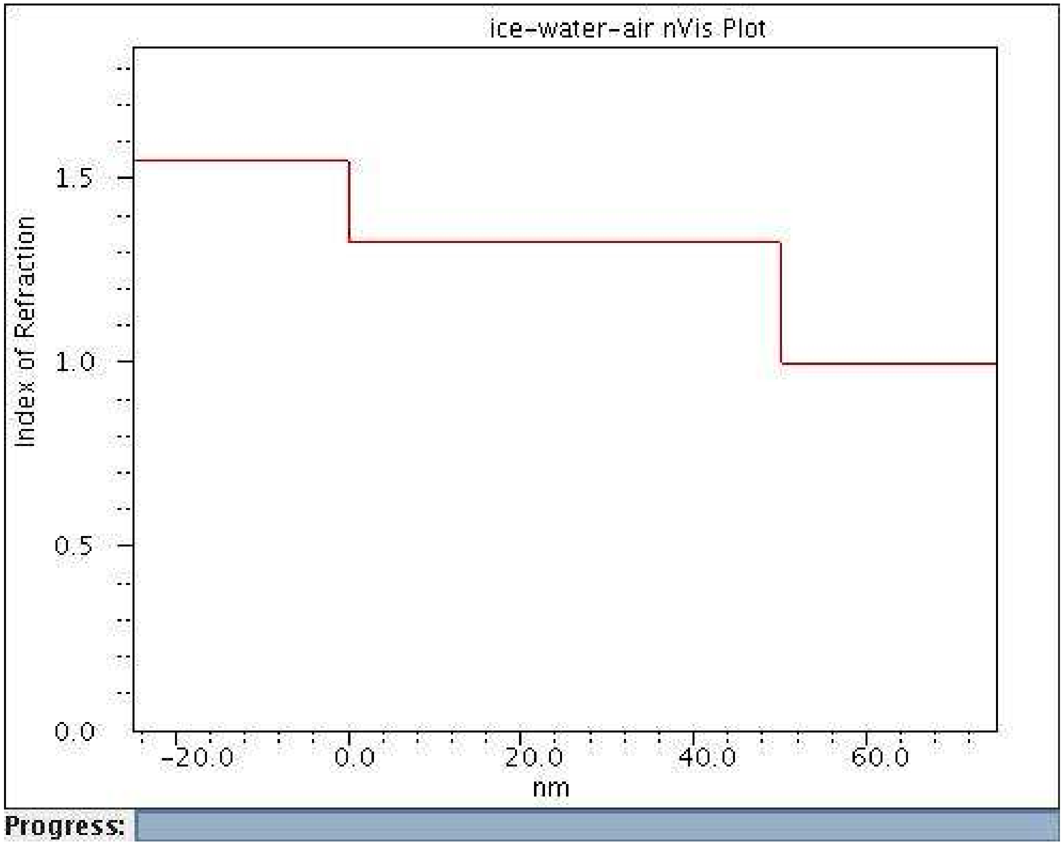


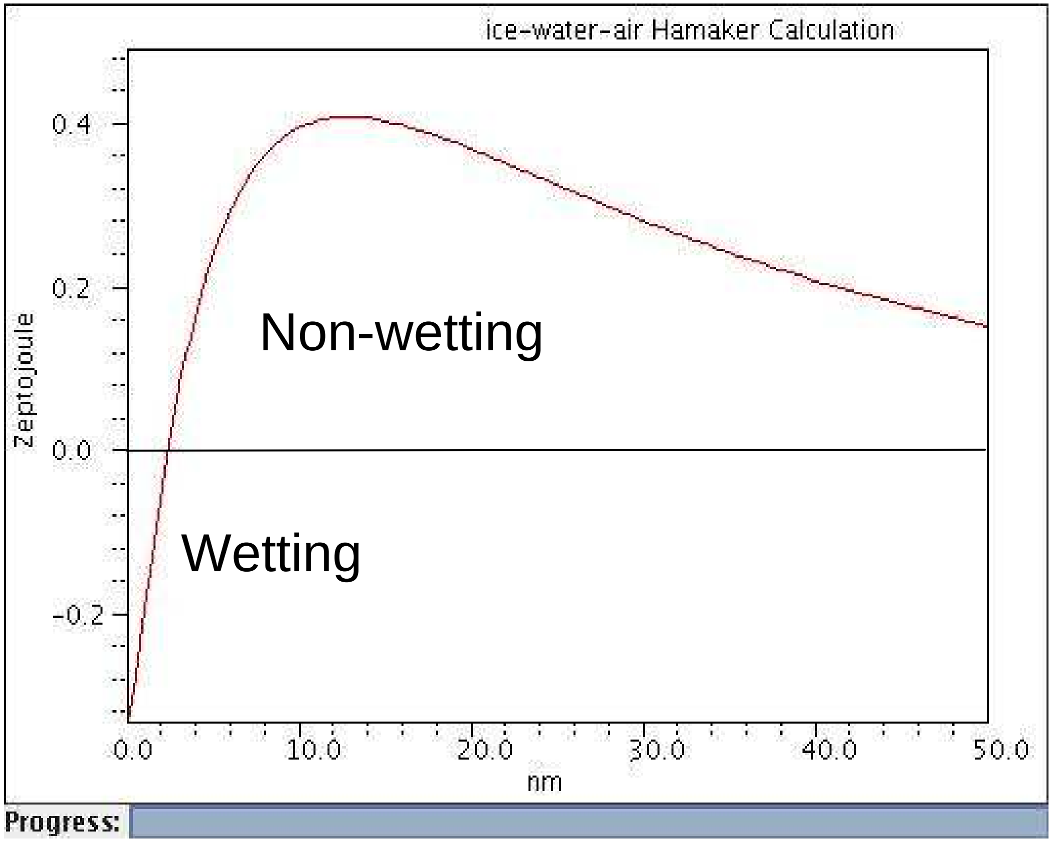
Name	Pai...	SPC	Comments	nVis	N...	DSPEC
al2o3-teels...	T U	al2o3-teel al2o3-teel	#?, Al2O3, alpha, sscor@Stutt VEELS, KK #?, Al2O3, alpha, sscor@Stutt VEELS, KK	1.76		☑
al2o3-vuv-p	T U	al2o3-vuv- al2o3-vuv-	Al2O3 Single Xtal Basal Plane VUV YO Al2O3 Single Xtal Basal Plane VUV YO	1.75		☑
aln-p	T U	aln-t aln-u	#301, AlN Single Xtal, Slack, w Ellips. #301, AlN Single Xtal, Slack, w Ellips.	2.14		☑
au-palik-p	T U	au-palik-t au-palik-u	au palik Au Palik	19....		☑
CIRCULOID	- -	- -	Interpolation Layer	0		☑
EMA	- -	- -	Interpolation Layer	0		☑
ice-d	T U	icedT icedU	:-LOs (.01,.08,.00)(.11,.05,.00)(.40, :-LOs (.01,.08,.00)(.11,.05,.00)(.40,	1.55		☑
LINEAR	- -	- -	Interpolation Layer	0		☑
mgal2o4-g...	T U	mgal2o4-g mgal2o4-g	#?, MgAl2O4 Spinel Geological, Burma, #?, MgAl2O4 Spinel Geological, Burma,	1.67		☑
mgal2o4-v...	T U	mgo-veels mgo-veels	#?, MgO, HM16-04-97-1, p0862o ref #?, MgO, HM16-04-97-1, p0862o ref	1.72		☑
mgo-veels-p	T U	mgo-veels mgo-veels	#?, MgO, HM16-04-97-1, p0862o ref #?, MgO, HM16-04-97-1, p0862o ref	1.72		☑
MIXTURE3	- -	- -	Interpolation Layer	0		☑
pd-palik-p	T U	pd-palik-t pd-palik-u	Pd Palik, ref. =S C Fain et al, Nanotech Pd Palik, ref. = S C Fain et al, Nanote	16....		☑
QUADRATIC	- -	- -	Interpolation Layer	0		☑
QUADROID	- -	- -	Interpolation Layer	0		☑
REVERSEQU...	- -	- -	Interpolation Layer	0		☑
	T	si3n4-t	#608SiN/glassGermany95%SiN			

current project: ice-water-air

Number	Material	nVis	Thickness	Dynamics
1	ice-d	1.55	-1	HalfSpace
2	water-	1.33	1	Center
3	vacuum-p	1	-1	HalfSpace

Equilibrium Surficial Film: A [Ice | Water | Air]





Index Of Refraction Profile

- Showing Steps In Index
- For Surficial Film On Ice

Retarded Hamaker Coefficient

- Novel Dispersion Interaction
- Wetting To Non-wetting Transition
  - With Surficial Film Thickness

Make State Of The Art Hamaker Calculations Available To All

- Open Source Program, Under GNU Public License

Controlled Wetting by Elec. Structure Doping

Electronic Structure and Dopants

- Glass Additives
  - Increase Index of Refr.
- Crossing Condition
  - London Dispersion Spectra
  - Equib. Surf. Films

Al_2O_3 | SiO_2 | Air

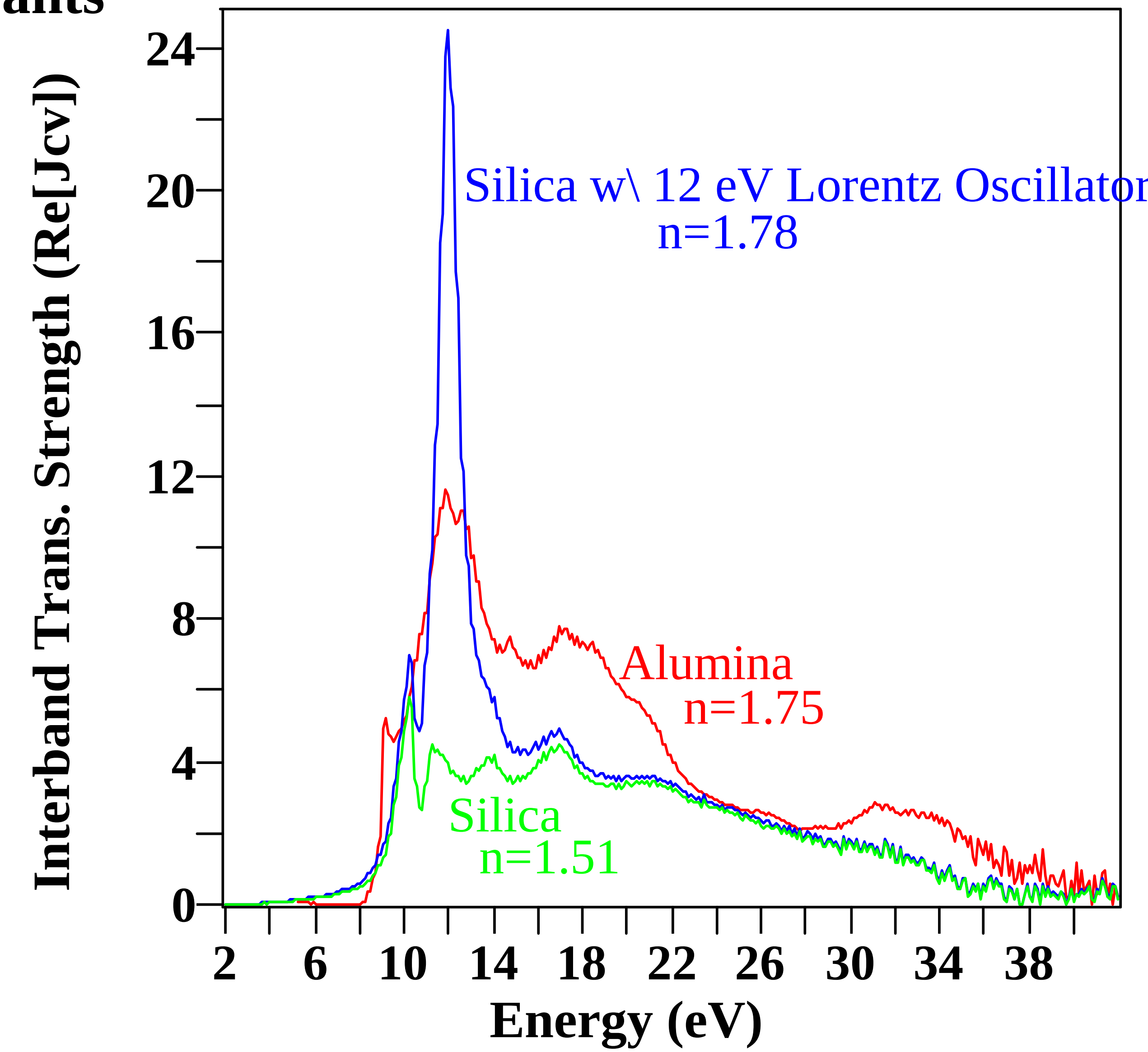
- Decreasing Indices
- Normal Wetting

Add Dopant at 12 eV Energy

- Increase Index of Refraction

Similar to Doping a Glass

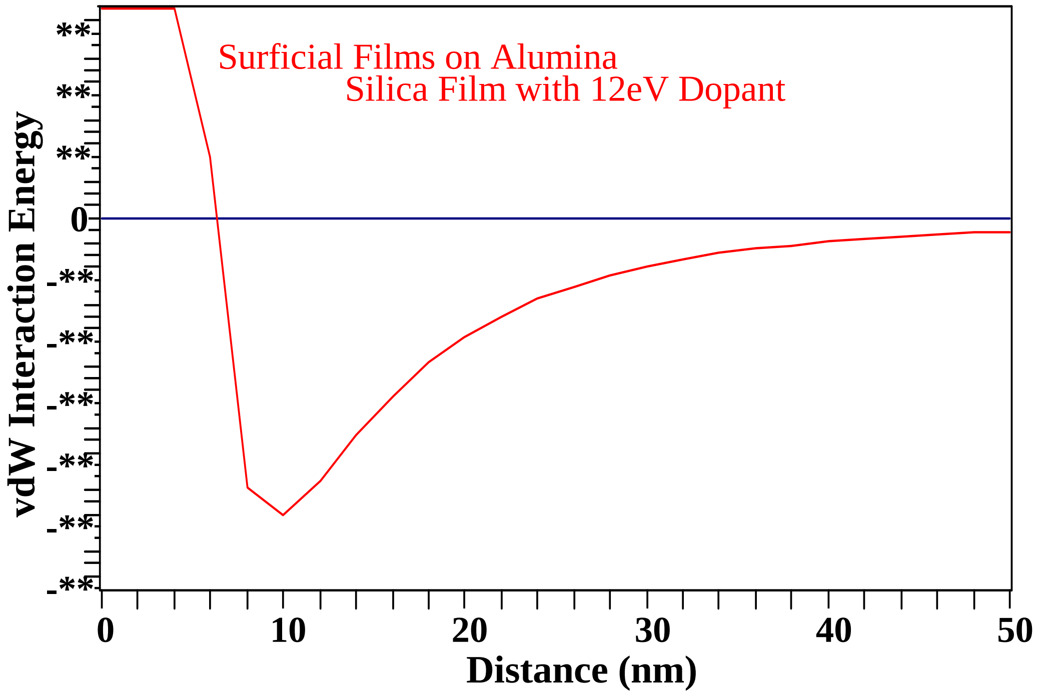
- Na, Ca, Ba,Y, La, Yb
- Exhibit Narrow Int. Band Tr.



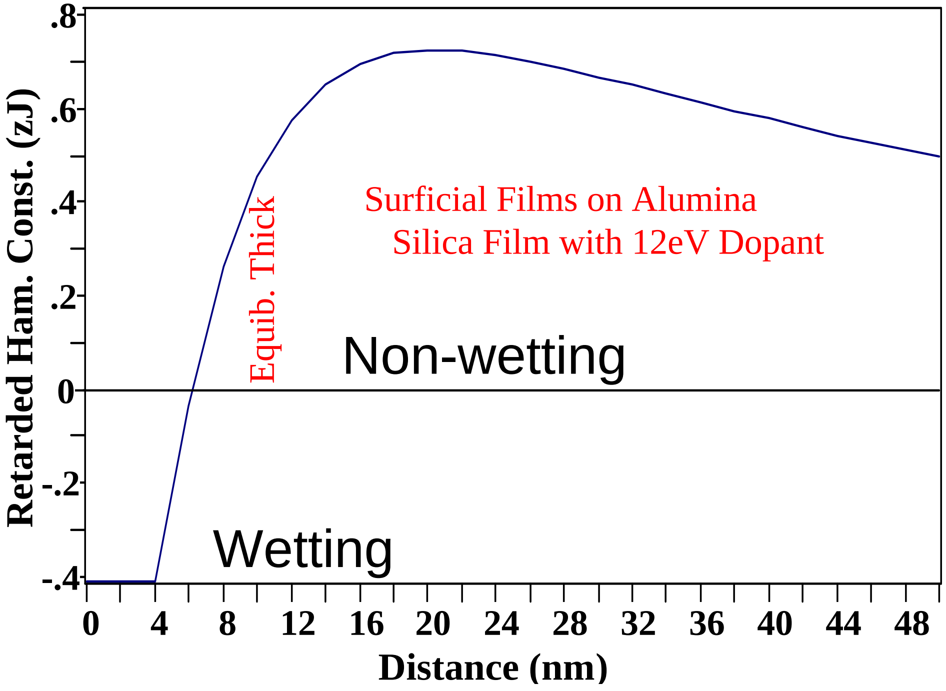
Control Of Dispersion Interactions By Electronic Structure & Chemistry

Equilibrium Surficial Films by ES Doping

Interaction Energy



Retarded Hamaker Constant



Equilibrium Surficial Film ↑

Al_2O_3 | SiO_2 with 12 eV Dopant | Air

Energy Minima, Zero Crossing of Hamaker Constant

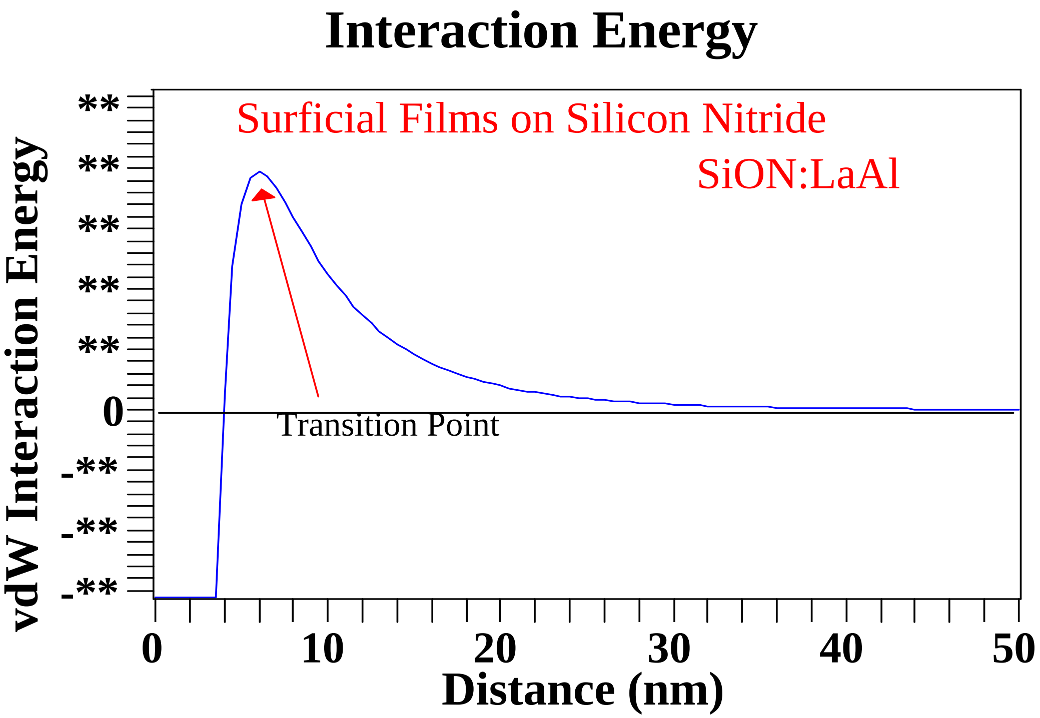
- Now Equilibrium Thickness Surficial Film
- Wetting of 1.75 with 1.78 Matl: Index “Rules “ Violated

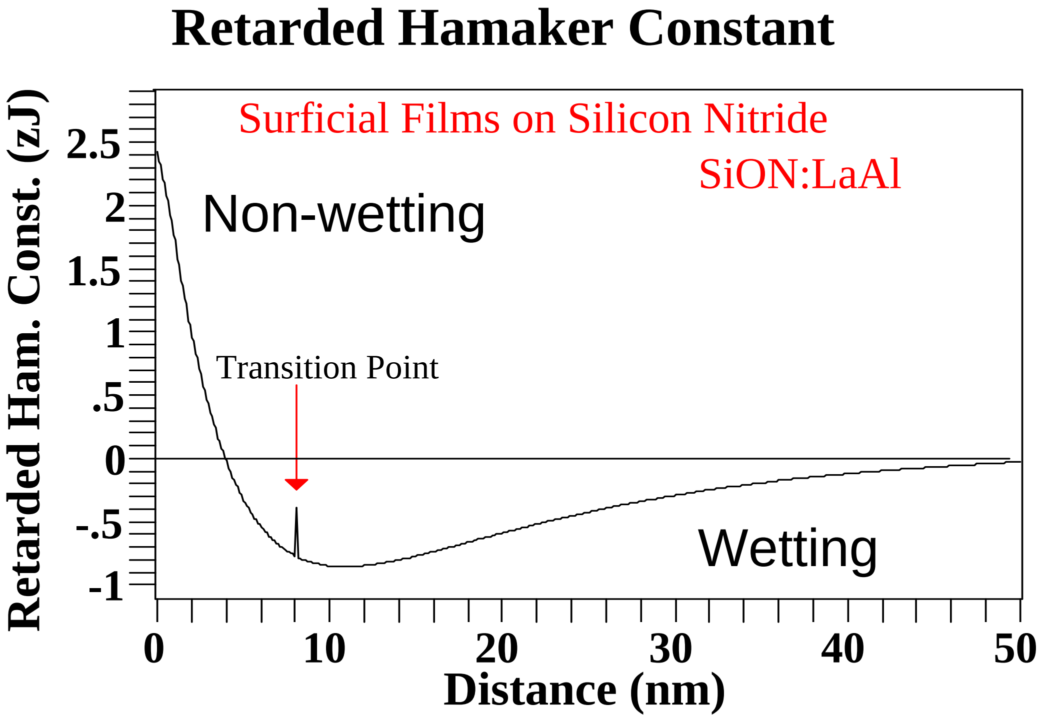
Design of Equib. Surficial Films By Doping

By Compositional Doping

Can Achieve Same
Wetting/Non-wetting Transition
As In Water And Ice

Bimodal: Nonwetting/Wetting





Bimodal: Nonwetting, With Wetting

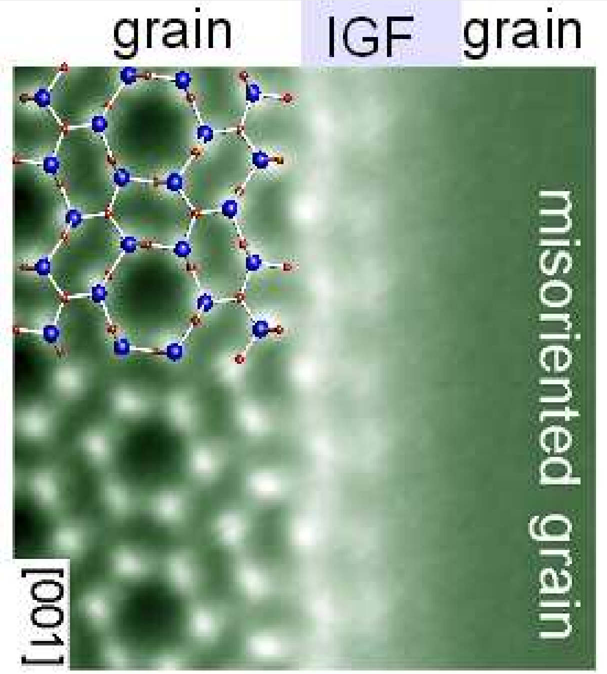
Different Condition From Equilibrium Surficial Film
- Note Zero Crossing & Curvature

Note Transition Point Thickness
- DeWetting Films Below Transition Point
- Metastable Wetting Films Above Transition Point Thickness

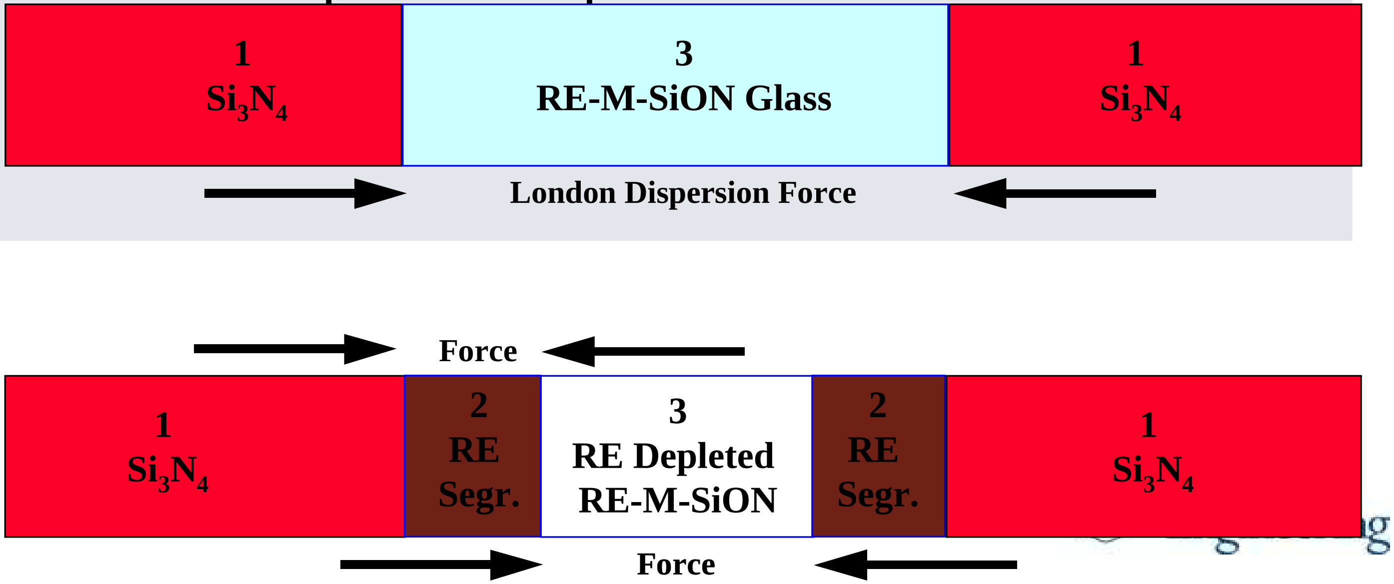
Useful for Microstructural Design

An Option For
“Lubricated Assembly”
With Snap-In
At Assembly Completion?

vdW-Ld Driven Rare Earth Segregation In RE-M-SiON: Si_3N_4



Coupled Compositional Variations



1
Si_3N_4

3
RE-M-SiON Glass

1
Si_3N_4

London Dispersion Force

Force

1
Si_3N_4

2
RE
Segr.

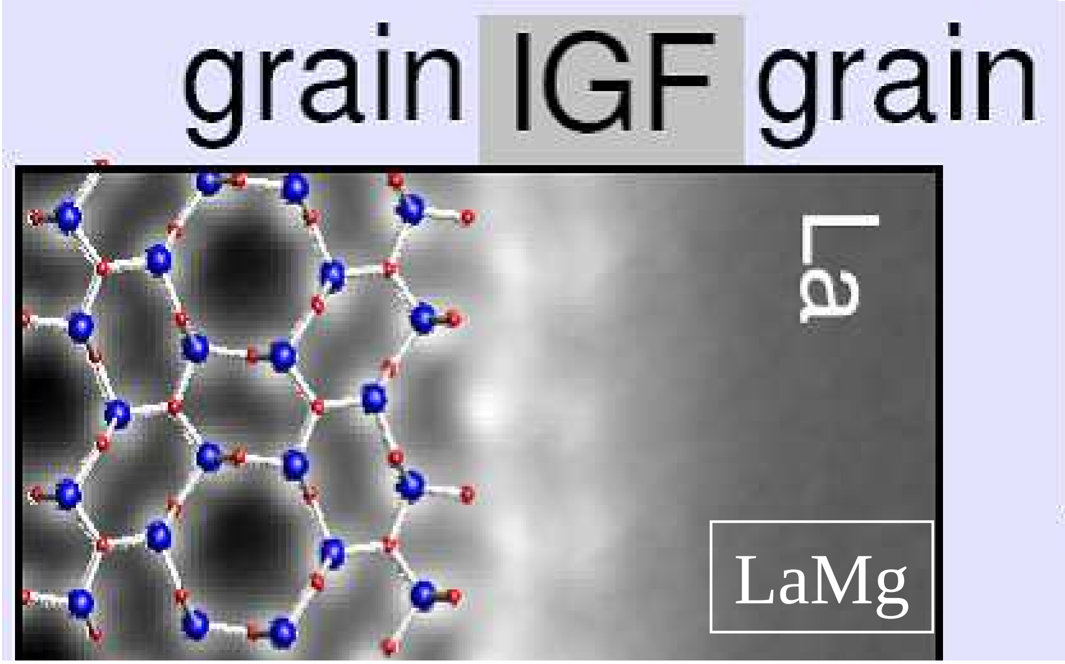
3
RE Depleted
RE-M-SiON

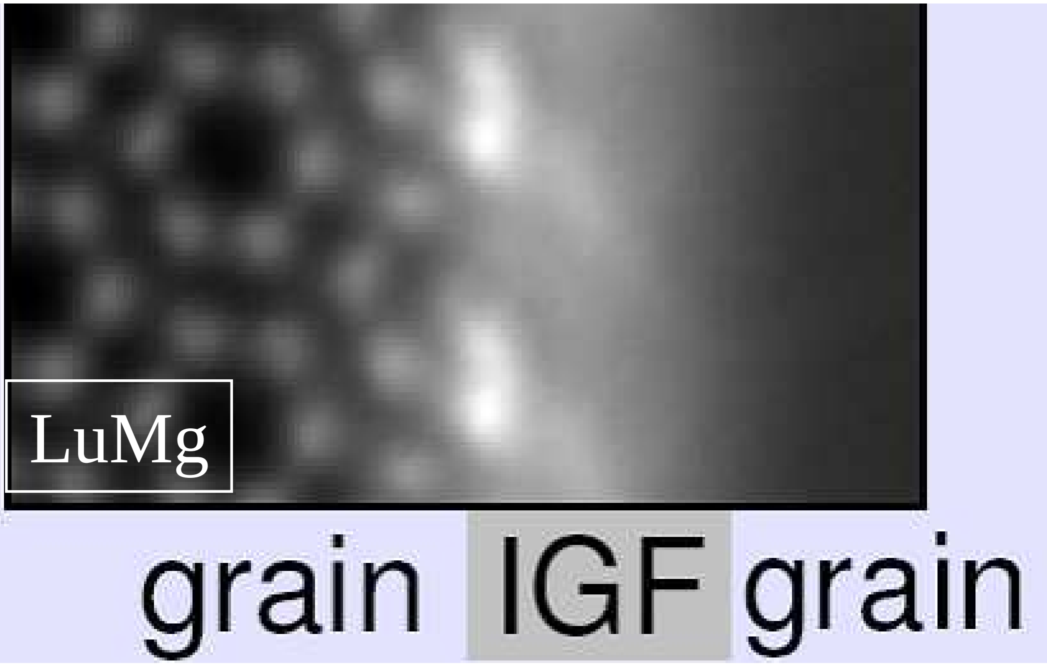
2
RE
Segr.

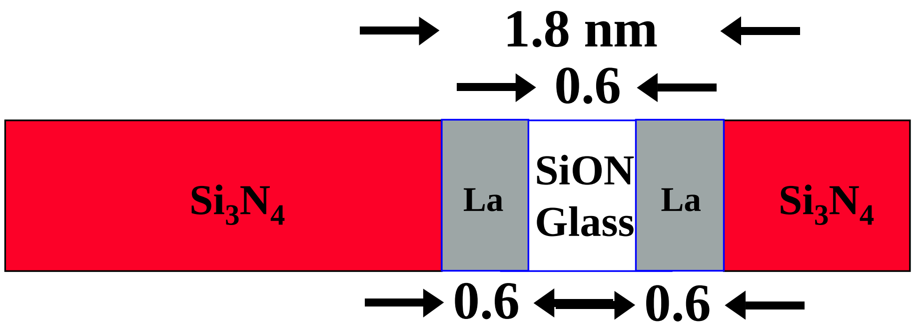
1
Si_3N_4

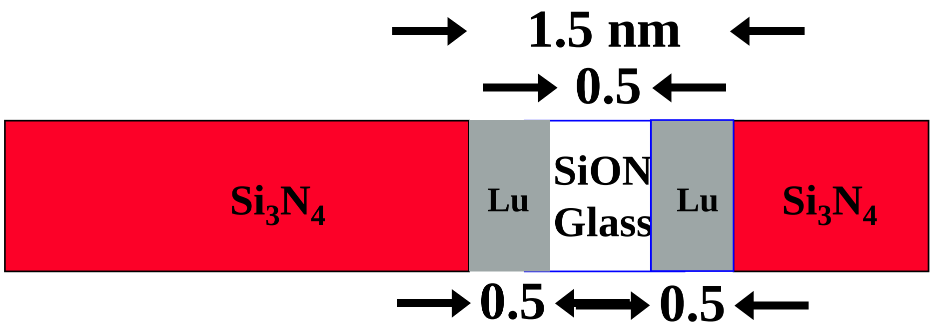
Force

Dimensions In Rare Earth-M-SiON:Si_3N_4 IGFs









LaMgSiON:Si_3N_4

1.8 nm Film Width

- 0.6 nm La Segregation Layers
- 0.6 nm Central Layer

LuMgSiON:Si_3N_4

1.5 nm Full Film Width

- 0.5 nm La Segregation Layers
- 0.5 nm Central Layer

Index Profiles Across Uniform & Segr. Interfaces

Homogenous IG Film

Interfacial RE Segr.

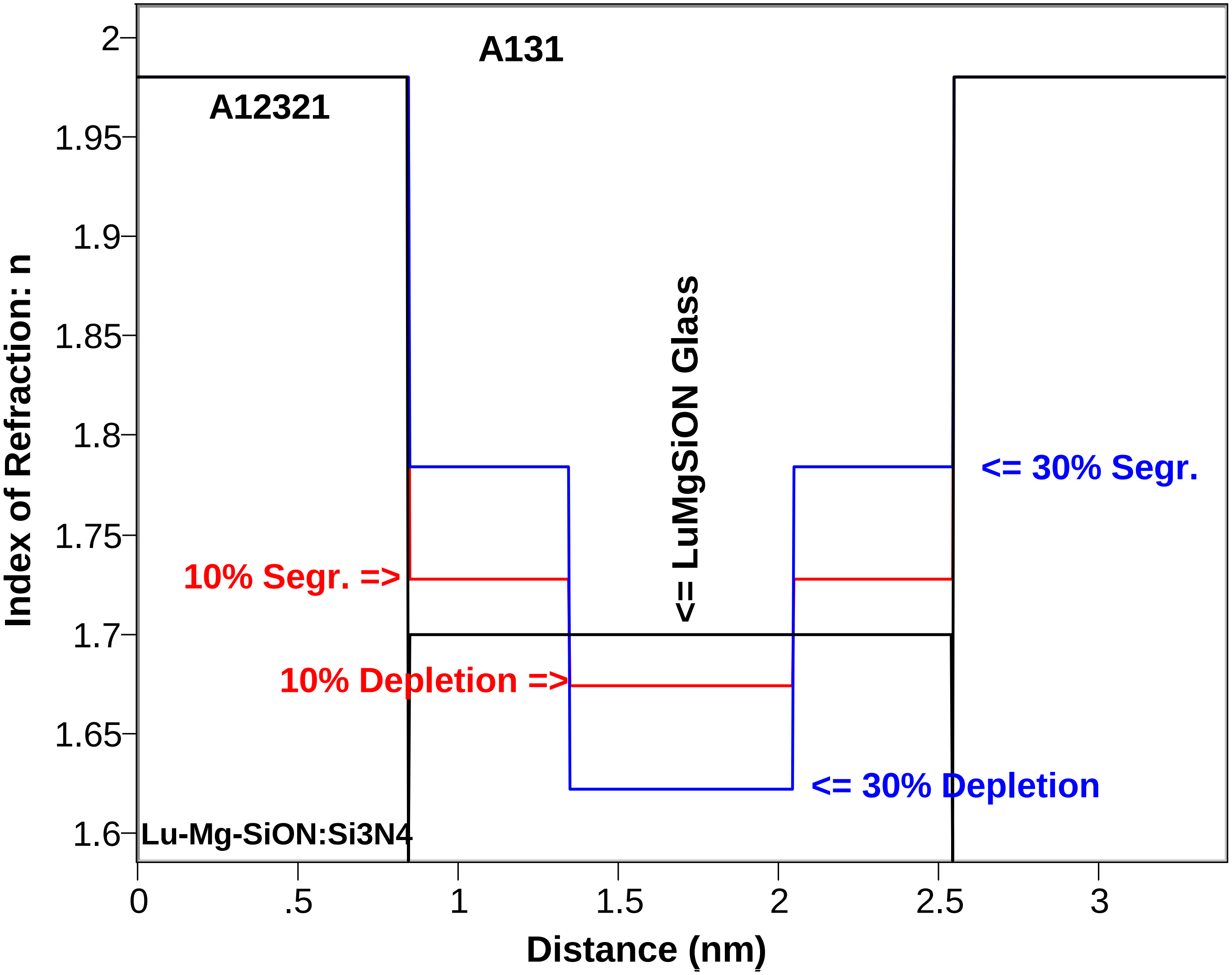
- Increases Index or Ref.
- At Interface

RE Interfacial Layer

- Shields Grains
- From Each Other

Study Two Levels

- 10 % Segregation
- 30% Segregation



1 Si_3N_4	2 RE Segr.	3 RE Depleted RE-M-SiON	2 RE Segr.	1 Si_3N_4

Depletion Layer (3) Ham. Coeff.

Non-Wetting Disp. Interaction

RE Segregation Reduces

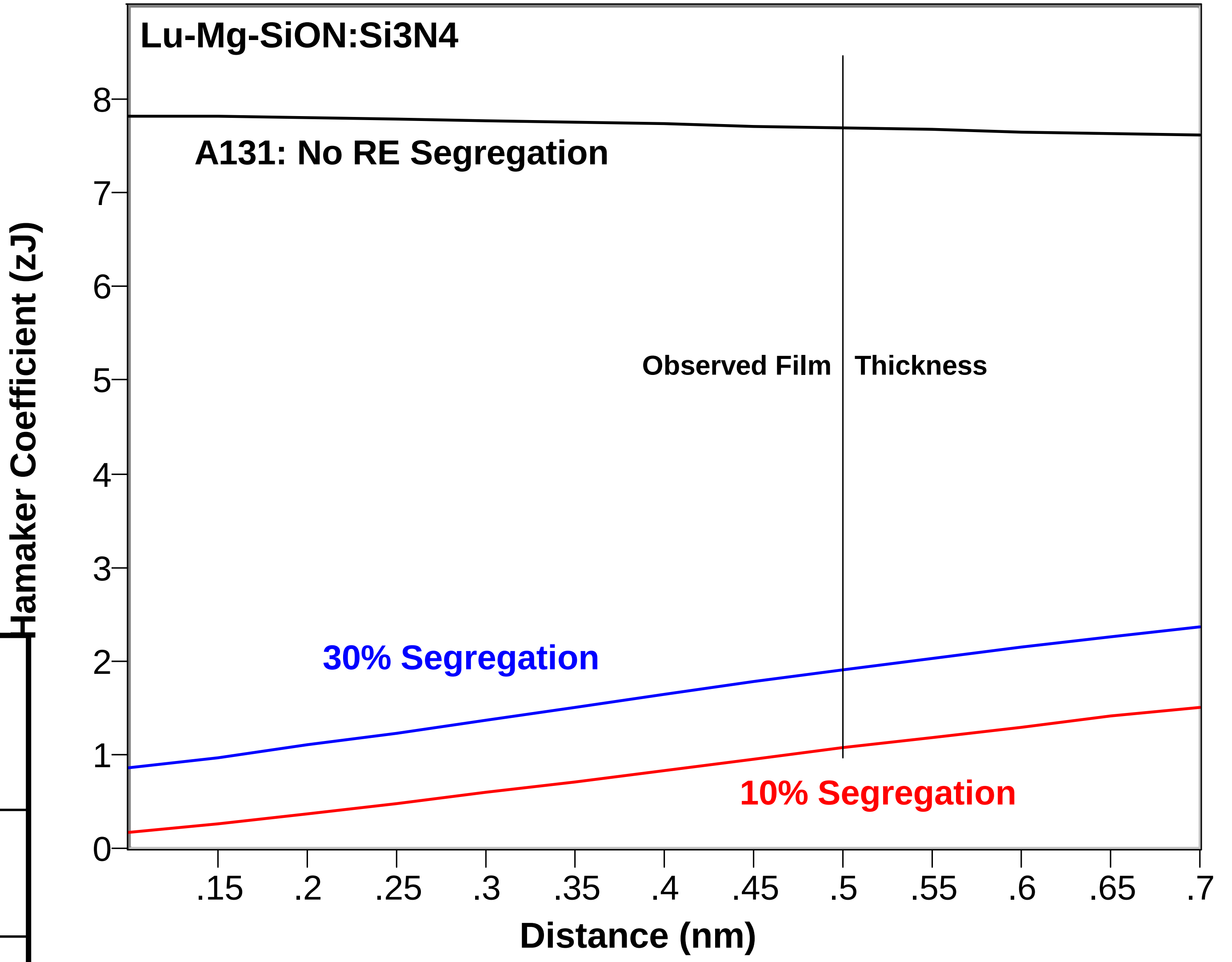
- Hamaker Coefficient
- London Interaction Energy

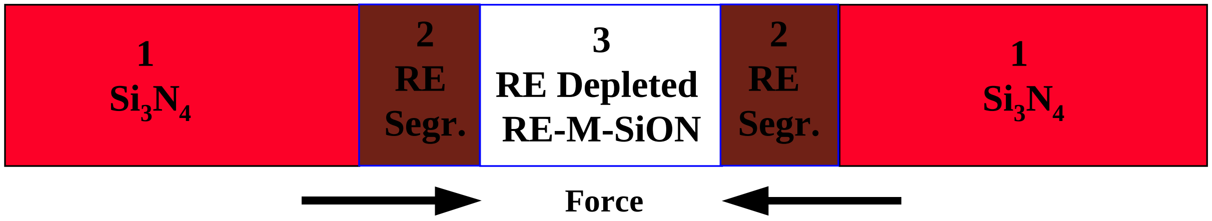
Depletion In SiON

- Dispersion Driven

Must Consider Whole System

$E_{L\,Disp.} = -\frac{A(l)}{12\pi l^2}$ **D_0=0.22 nm**	Hamaker Coeff. A (zJ)	London Energy (mJ/m^2)
No RE Segr.	**7.2**	**4.0**
10% Segr.	**1.1**	**0.6**
30% Segr.	**1.9**	**1**





1
Si_3N_4

2
RE Segr.

3
RE Depleted RE-M-SiON

2
RE Segr.

1
Si_3N_4

Force

Segregation Layer (2) Ham. Coeff.

Wetting To Non-Wetting Transition

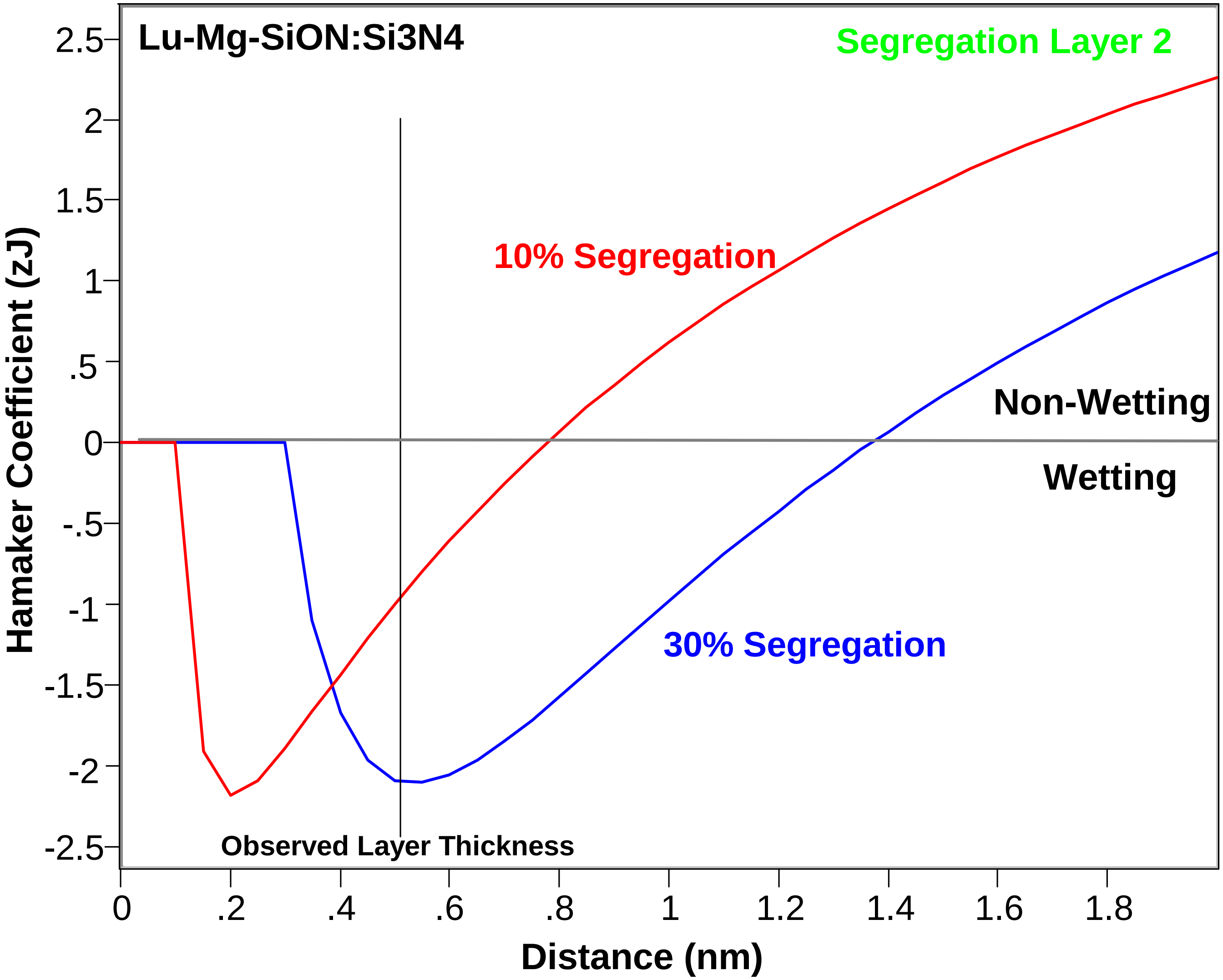
Thickness Dependent Wetting Transition

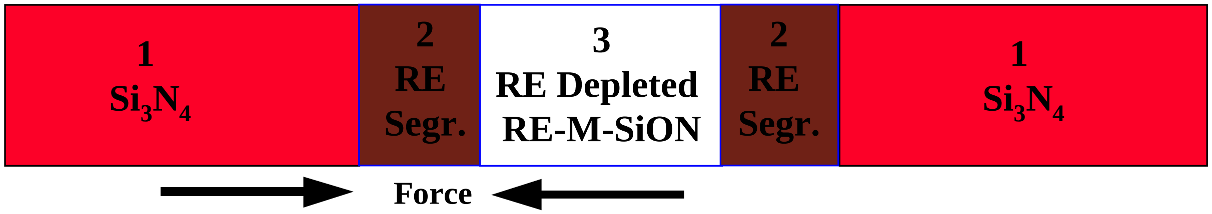
Compare To Water On Ice

- Equilibrium Water Film
- Lond. Dispersion Stabilized
- See Elbaum, Schick PRL

RE Segregation Driven

- By Increased Index
- In Segr. Layer




1 Si$_3$N$_4$

2 RE Segr.

3 RE Depleted RE-M-SiON

2 RE Segr.

1 Si$_3$N$_4$

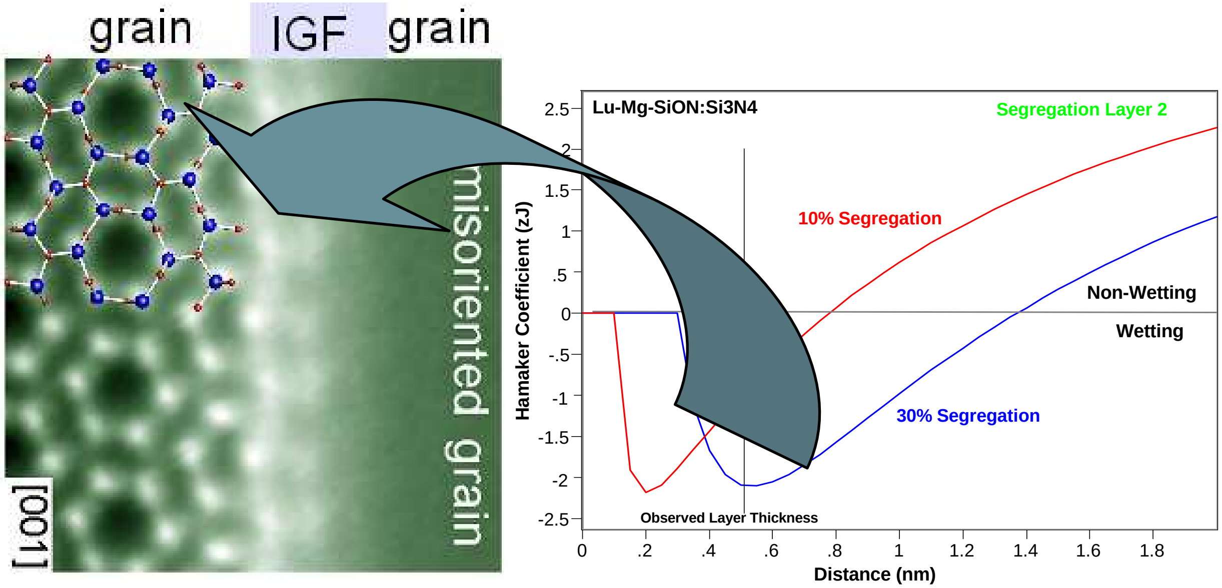
Force

Dispersion Driven Interfacial RE Segregation

RE Segr. Coupled System
- With RE Depletion In Center
- RE Segregation To Interface

Equilibrium Layer Configuration
- London Dispersion Stabilized

Comparable To Lu Segr. In Si_3N_4



Combined Disp. Energy
- Of Segr Layer
- And Depletion Layer

Lowers Dispersion E
- **Of Intergranular Film**

	Depletion Layer 3 (SiON Center)		Segr. Layer 2 (Si_3N_4 Interface)		Total Disp. Energy mJ/m^2 $E_{L\,Disp.} = -\frac{A(l)}{12\pi l^2}$
	A (zJ)	Lond. E (mJ/m^2)	**A (zJ)**	Lond. E (mJ/m^2)	
No RE Segr.	**7.2**	4,0			4.0
10% Segr.	**1.1**	0.6	**-1**	-0.6	0
30% Segr.	**1.9**	1	**-2.1**	-1.2	-0.2

Conclusions

Long Range Interactions In Nanoscale Science

- **Electrodynamics:** vdW-L Dispersion
- **Electrostatics**
- **Polar Interactions**

$SrTiO_3$ Grain Boundary Dispersion Energies

- Reduced Physical & Electron Density
- ~ 5 to 10% of Chemical GB Energy

Novel Wetting Conditions

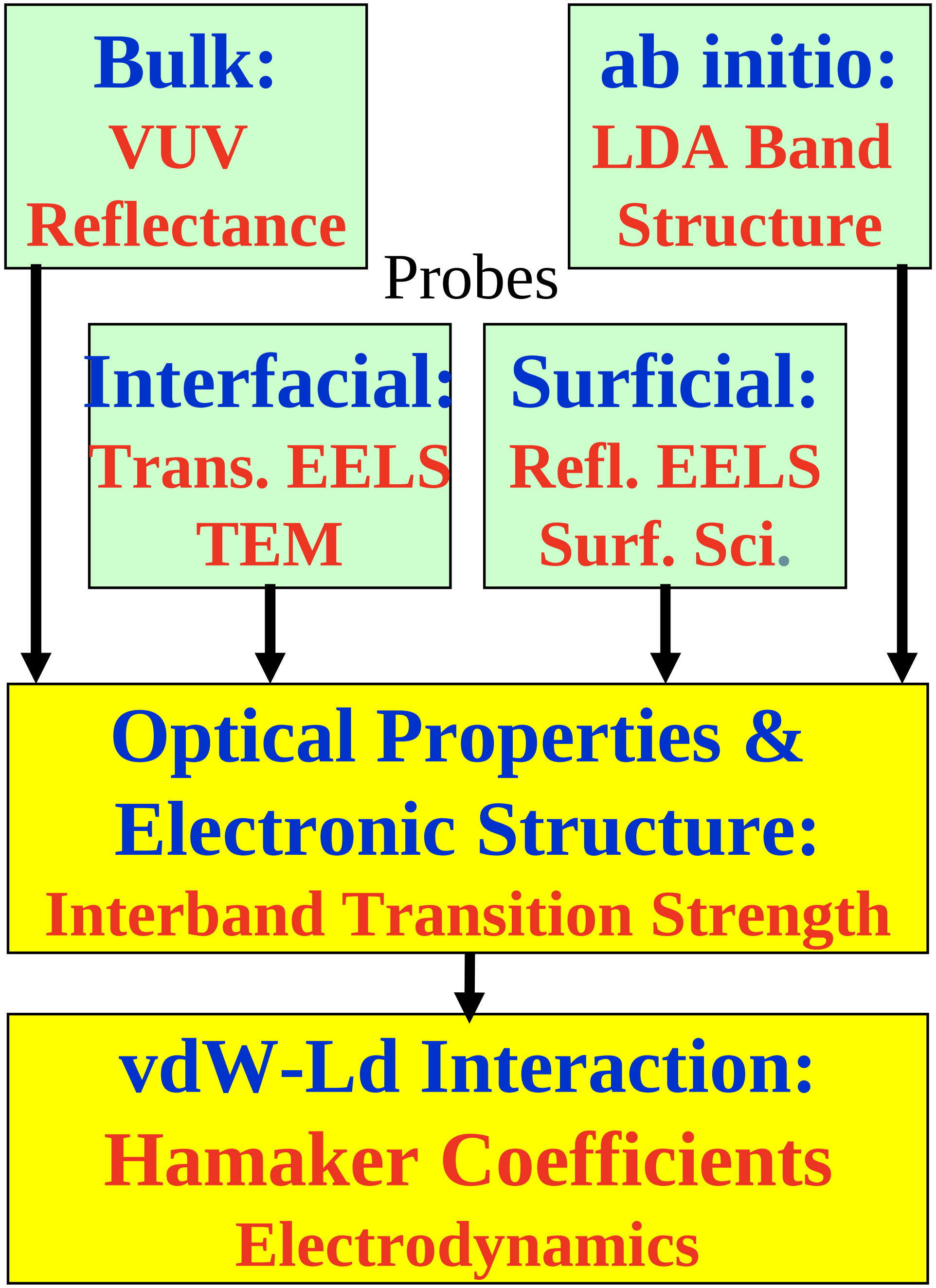
- Wetting/Non-wetting Transitions: Premelting
- Non-wetting/Wetting Transitions:
  - Lubricated Assembly?

Dispersion Driven Interfacial Segregation

- But What About The Electrostatic Energy

New Non-Plane Parallel Hamaker Development

- Carbon Nanotubes



Bulk: VUV Reflectance

ab initio: LDA Band Structure

Probes

Interfacial: Trans. EELS TEM

Surficial: Refl. EELS Surf. Sci.

Optical Properties & Electronic Structure: Interband Transition Strength

vdW-Ld Interaction: Hamaker Coefficients Electrodynamics