Solving Nanoscience Problems Using High Performance Computing

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Oak Ridge National Laboratory
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Vanderbilt Center for Integrative Cancer Biology
Vanderbilt University Medical School

Advanced Scientific Computing Advisory Committee Meeting

ORAU Technology Center

November 3-4, 2009

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Outline

- Introduction
  - *Theory, modeling and simulation in nanoscience*
  - *Center for Nanophase Materials Sciences at Oak Ridge National Laboratory*
- Interpretation of complex phenomena in experiment
  - *AFM experiment*
  - *TiO_2 nanoparticles via DFT (density functional theory)*
  - *Nanoscale complexity in electrical double layer*
- Design of new nanostructured materials and systems based on emergent phenomena at nanoscale
  - *Nanotube networks*
- Fundamental insight into emergent phenomena at nanoscale
  - *Fluctuations at the nanoscale*
  - *Rupture of Au nanowires*
- Conclusions

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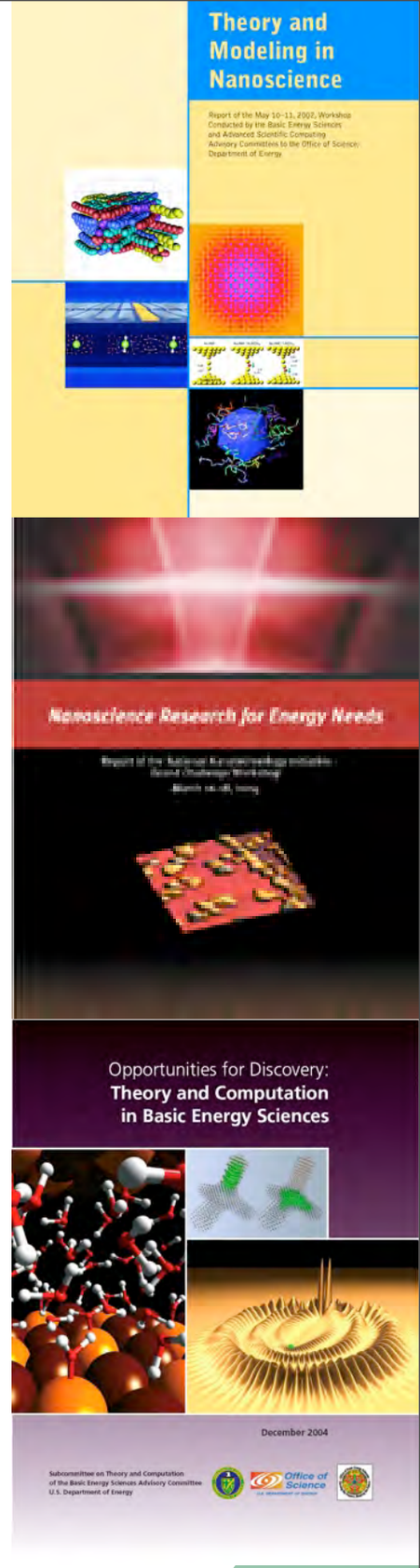
Introduction

- Theory, modeling and simulation (TMS)
  - *Expected to play key role in nanoscale science and technology*
    - "Nanotechnology Research Directions: IWGN Workshop Report. Vision for Nanotechnology Research and Development in the Next Decade," edited by M.C. Roco, S. Williams, P. Alivisatos, Kluwer Academic Publisher, 2000
      - *Also available on-line at http://www.wtec.org/loyola/nano/IWGN.Research.Directions/*
    - McCurdy, et al. "Theory and Modeling in Nanoscience: Report of the May 10-11, 2002, Workshop Conducted by the **Basic Energy Sciences and Advanced Scientific Computing Advisory Committees** of the Office of Science, Department of Energy
      - *Published by DOE*
      - *Also available on the web at http://www.er.doe.gov/bes/reports/files/TMN_rpt.pdf*
    - Alivisatos, et al., "Nanoscience Research for Energy Needs: Report of the March 2004 National Nanotechnology Initiative Grand Challenge Workshop
      - *Published by DOE and NNI*
      - *Also available on the web at http://www.er.doe.gov/bes/reports/files/NREN_rpt.pdf*
    - BESAC, "Opportunities for Discovery: Theory and Computation in Basic Energy"
      - *Published by DOE*
      - *Also available on the web at http://www.er.doe.gov/bes/reports/files/OD_rpt.pdf*



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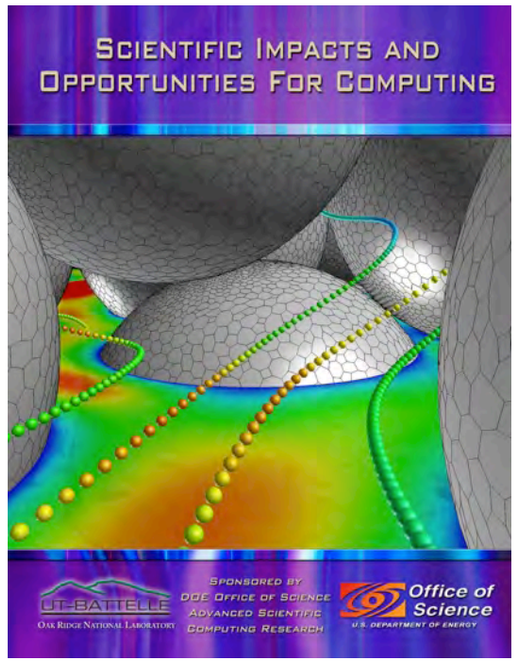
Introduction

- Theory, modeling and simulation (TMS)
  - McCabe *et al.*, "Scientific Impacts And Opportunities For Computing," report of workshop held January 9 -12, 2008, sponsored by the Advanced Scientific Computing Advisory Committees of the Office of Science, Department of Energy
    - *Also available online at http://www.sc.doe.gov/ascr/ProgramDocuments/Docs/ScientificImpacts&Oppor.pdf*



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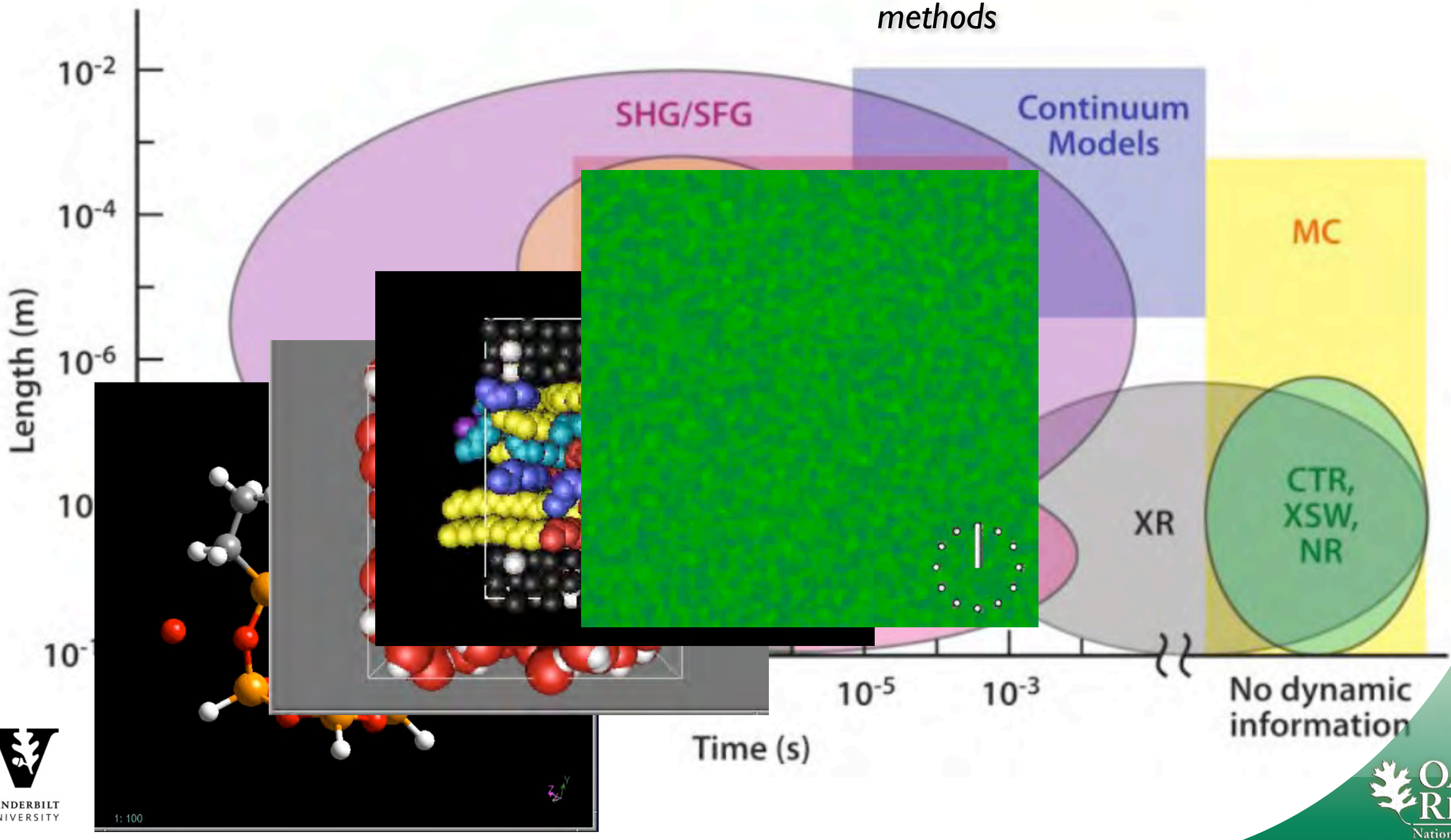
Introduction

- Hierarchy of TMS methods relevant to nanoscale science and technology
  - *Along with some corresponding experimental methods*



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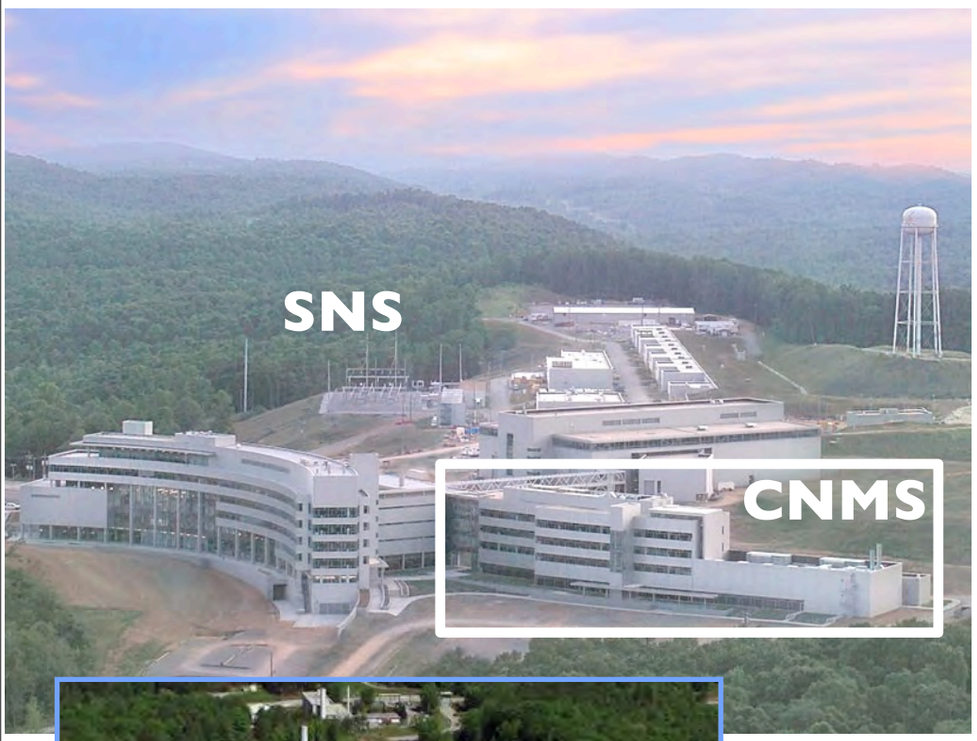
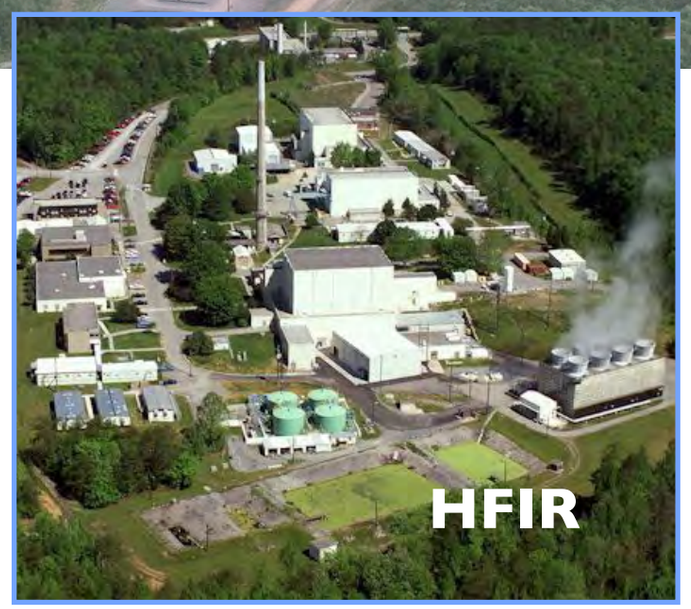
Center for Nanophase Materials Sciences

Oak Ridge National Laboratory

Focuses in neutron science, synthesis science, and theory/modeling/simulation





- Neutron Science
  - *Opportunity to use unique neutron scattering capabilities to understand nanoscale materials and processes*
- Synthesis Science
  - *Science-driven synthesis will be the enabler of new generations of advanced materials*
- Theory/Modeling/Simulation
  - *The Nanomaterials Theory Institute*
- Access to other major ORNL facilities
  - *Spallation Neutron Source (SNS)*
  - *High-Flux Isotope Reactor (HFIR)*
  - *National Center for Computational Sciences (NCCS)*

Center for Nanophase Materials Sciences web site http://cnms.ornl.gov

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TMS in Nanoscience

- Theoretical and computational nanoscience
  - *Have played, and continue to play, central role in nanoscience*
  - *TMS play greater role in nanoscience than in macroscopic materials and chemical sciences*
    - Many experiments performed at the nanoscale can only be interpreted through theory
    - TMS can provide a convenient framework to isolate effects and phenomena in a way that may be difficult or impossible to achieve in an experiment
      - *Boundary and initial conditions are under complete control, which may be impossible to achieve in experiment*
      - *TMS is crucial in understanding emergent phenomena in nanoscale systems*
    - TMS can be used to design new nanostructured materials, as well as systems based on nanoscale phenomena
- By design and from beginning, theoretical and computational nanoscience play central role at CNMS
  - *Large number of user projects (about 25% of total)*
  - *Strong interaction with computational scientists*

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Integration of Computing and Nanoscience at ORNL CNMS and CSMD

- Beginning with original proposal....
  - *Strong TMS component*
    - Nanomaterials Theory Institute
  - *Strong interconnection and collaboration between CNMS and CSMD*
    - Budget for CNMS to fund joint activities with CSMD
    - Thomas Schulthess hired as joint group leader for CNMS Nanomaterials Theory Institute and CSMD Computational Materials Group
    - Gonzalo Alvarez, Thomas Maier, Jeremy Meredith, and Michael Summers partially funded by CNMS to target big nanoscience applications
      - *Computational endstation for nanoscience*
    - Unique capabilities (e.g., VASP code efficient on petascale platforms)
- 2008 Gordon Bell Prize
  - *Multi-teraflops Simulations of Disorder Effects on the Transition Temperature of the High Tc Superconducting Cuprates*
    - Alvarez, G., D'Azevedo, E. F., Eisenbach, M., Kent, P., Larkin, J. M., Levesque, J. M., Maier, T. A., Maxwell, D. E., Meredith, J., Schulthess, T. C., Summers, M. S.

A win-win for CNMS and CSMD!

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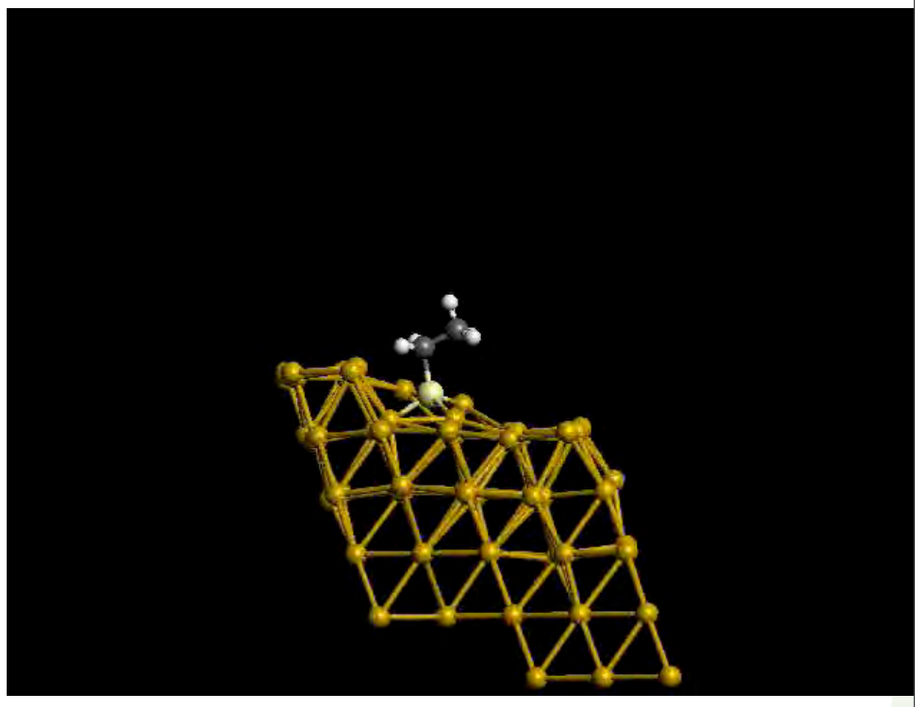
Role of Theory, Modeling and Simulation (TMS) in Nanoscience

- Interpretation of complex phenomena in experiment

Interplay of TMS and Experiment - Examples

- Interpretation of AFM experiment
  - *Many experiments at the nanoscale require TMS to understand what is being measured*



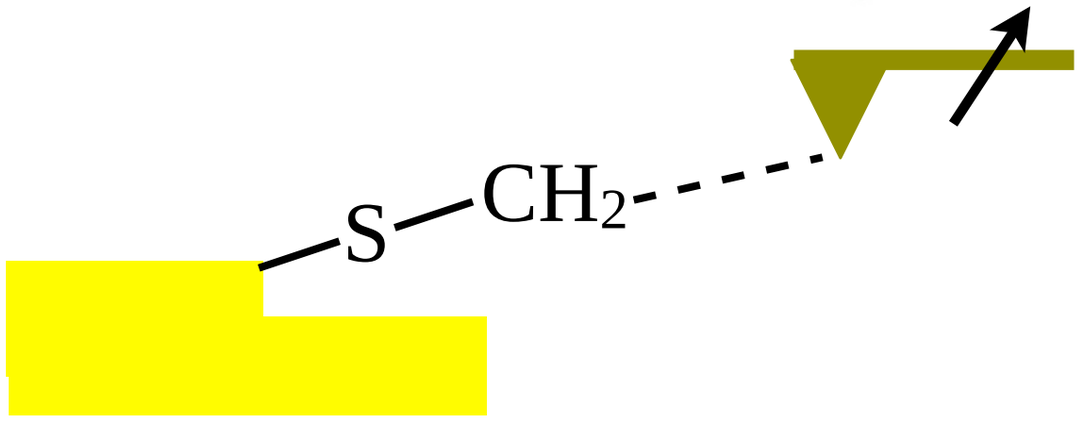
VOLUME 89, NUMBER 18 PHYSICAL REVIEW LETTERS 28 OCTOBER 2002

Pulling Monatomic Gold Wires with Single Molecules: An *Ab Initio* Simulation

Daniel Krüger,[1] Harald Fuchs,[1] Roger Rousseau,[2] Dominik Marx,[2] and Michele Parrinello[3]
[1]*Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm Klemm-Strasse 10, 48149 Münster, Germany*
[2]*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany*
[3]*Swiss Center for Scientific Computing/ETH Zurich, Via Cantonale, Galleria 2, 6928 Manno (TI), Switzerland*
(Received 30 April 2002; published 10 October 2002)

Car-Parrinello molecular dynamics simulations demonstrate that pulling a single thiolate molecule anchored on a stepped gold surface does not preferentially break the sulfur-gold chemical bond. Instead, it is found that this process leads to the formation of a monoatomic gold nanowire, followed by breaking a gold-gold bond with a rupture force of about 1.2 nN. The simulations also indicate that previous single-molecule thiolate-gold and gold-gold rupture experiments both probe the same phenomenon, namely, the breaking of a gold-gold bond within a gold nanowire.

DOI: 10.1103/PhysRevLett.89.186402 PACS numbers: 71.15.Pd, 62.25.+g, 82.37.Gk



Unifies two prior experimental results:
- Au-Au bond in nanowire - Rubio-Bollinger et al., *Phys. Rev. Letts.* **87** (2001) 026101
- Au-S "bond" measured at Au surface - Grandbois, *Science* **283** (1999) 1727-1730

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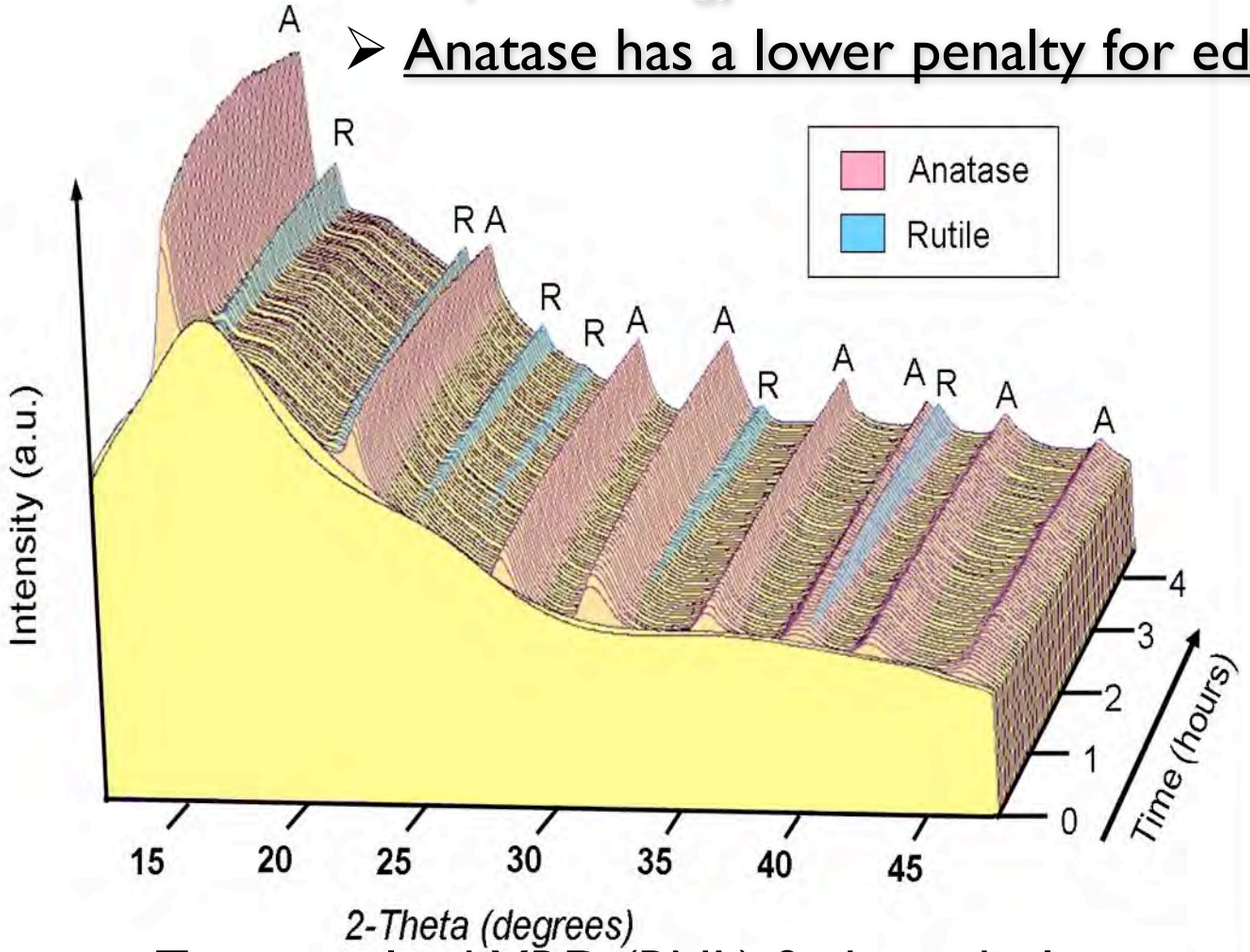
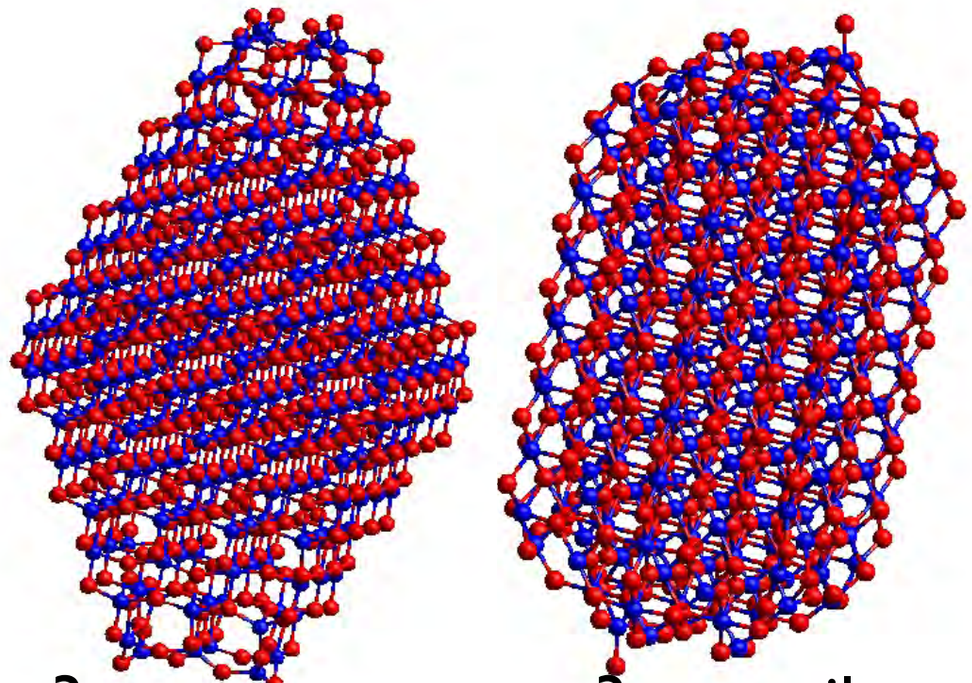
Determining Stability of TiO_2 Nanoparticles Using DFT and XRD

- Relative stability of rutile and anatase
  - *Rutile is most stable TiO_2 phase; anatase is often seen and is most stable at nanoscale*
  - *Large scale DFT calculations reveal the importance of edge and defect contributions to the surface energy*
    - ➢ Anatase has a lower penalty for edges than rutile since bulk is already distorted



Time resolved XRD (BNL) finds gradual development of rutile from majority anatase



3nm anatase 3nm rutile

Benchmark DFT calculations (NERSC & NCCS) finds similar surface energies for 3nm particles. Anatase is strongly favored for smaller sizes.

Classical MD: Naicker *et al.*, *J. Phys. Chem. B* **109** (2005) 15243
DFT & XRD: Hummer *et al. J. Phys. Chem C* **113** (2009) 4240

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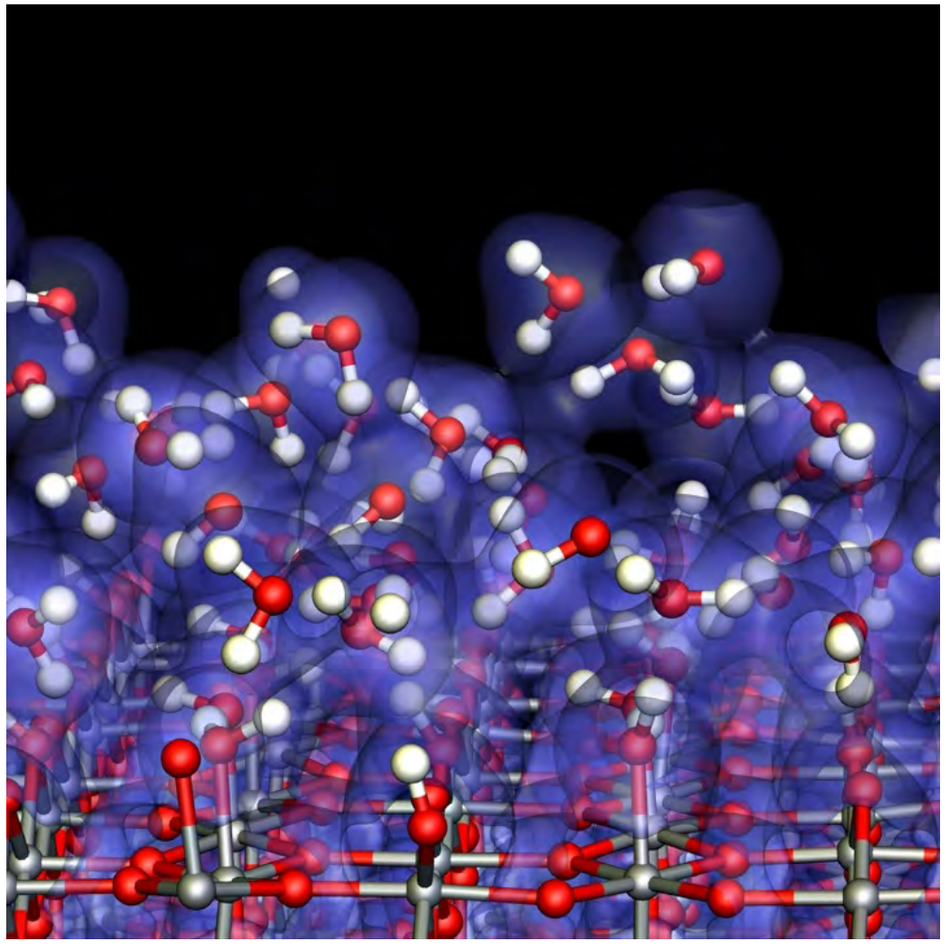
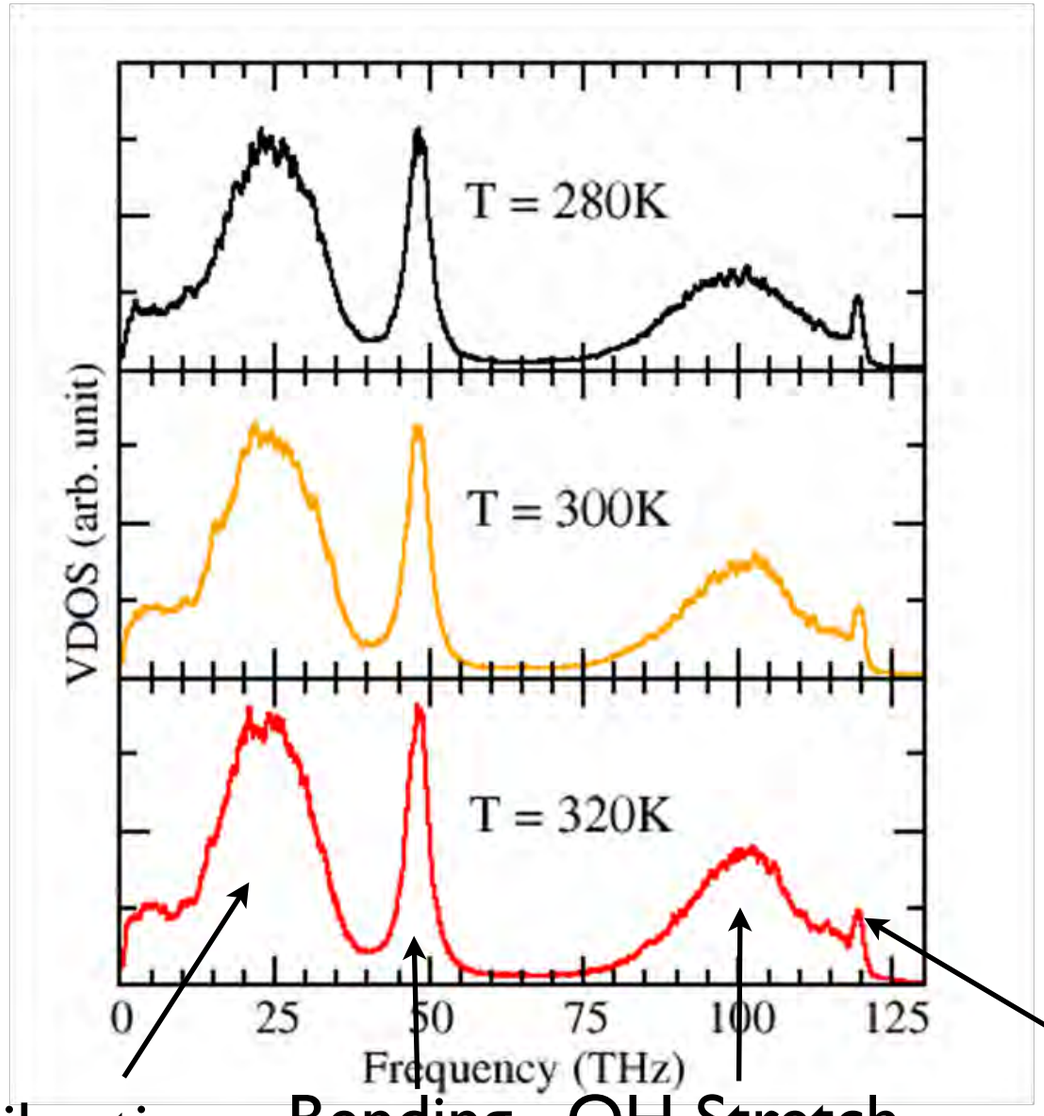
Determining Properties of Water at Oxide Surfaces

- Detailed information on structure (adsorption, protonation/dissociation level) of water on (110) rutile
  - *Large scale DFT simulations are validated using x-ray and neutron scattering data. Calculations are being extended to other oxide/mineral surfaces.*





Kumar *et al. J. Phys. Chem.* C., **13** (2009) 13732-13740

Practical Applications

Contam. Trans./Remediation
Catalysts, Fuel Cells
Materials Synthesis
Power Plant Operations

Synchrotron XSW, CTR, EXAFS

[1]Fenter, [2]Zhang, [3]Sturchio, [1]Cheng, [2]Bedzyk
([1]ANL, [2]Northwestern, [3]UIC)

Second Harmonic Generation

Fitts, Eisenthal, Heinz (Columbia/EMSI)

pH-Titrations/Ion Adsorption

[1]Ridley, [2]Wesolowski, [2]Benezeth,
[2]Palmer, [2]Anovitz ([1]Texas Tech, [2]ORNL)

Microelectrophoresis

Lvov, Fedkin, Zhou (Penn State)

Classical EDL Models

MUSIC Model

[1]Machesky, [2]Ridley
([1]Ill. St. Water Surv., [2]Texas Tech)

Molecular Dynamics Simulations

[1]Predota, [2]Chialvo, [3]Cummings
([1]Czech Ac.Sci., [2]ORNL, [3]Vanderbilt/ORNL)

***Ab Initio* Molecular Modeling**

[1]Kubicki, [2]Bandura, [1]Sykes
([1]Penn State, [2]St. Petersburg)

"Chemical Reality"

Predictable/Transferable
Mechanisms/Rates
Quantum effects
Model-Independent

Nanoscale Complexity at the Electrical Double Layer

Goal of Simulation Studies

- Carry out large scale molecular dynamics simulations taking into account atomistic nature of the surface
- Provide microscopic details of the structure of electric double layer and mechanisms at the interface
  - *More realistic and sophisticated model of EDL*
  - *Comparison with X-ray measurement - 3D structural map*
- Study dependence of interfacial properties on surface charge (pH)
  - *Input of parameters from titration measurements and classical models of electric double layer (EDL)*
- Study dynamic and electrostatic properties of EDL
  - *Interpretation of electrokinetic measurements*

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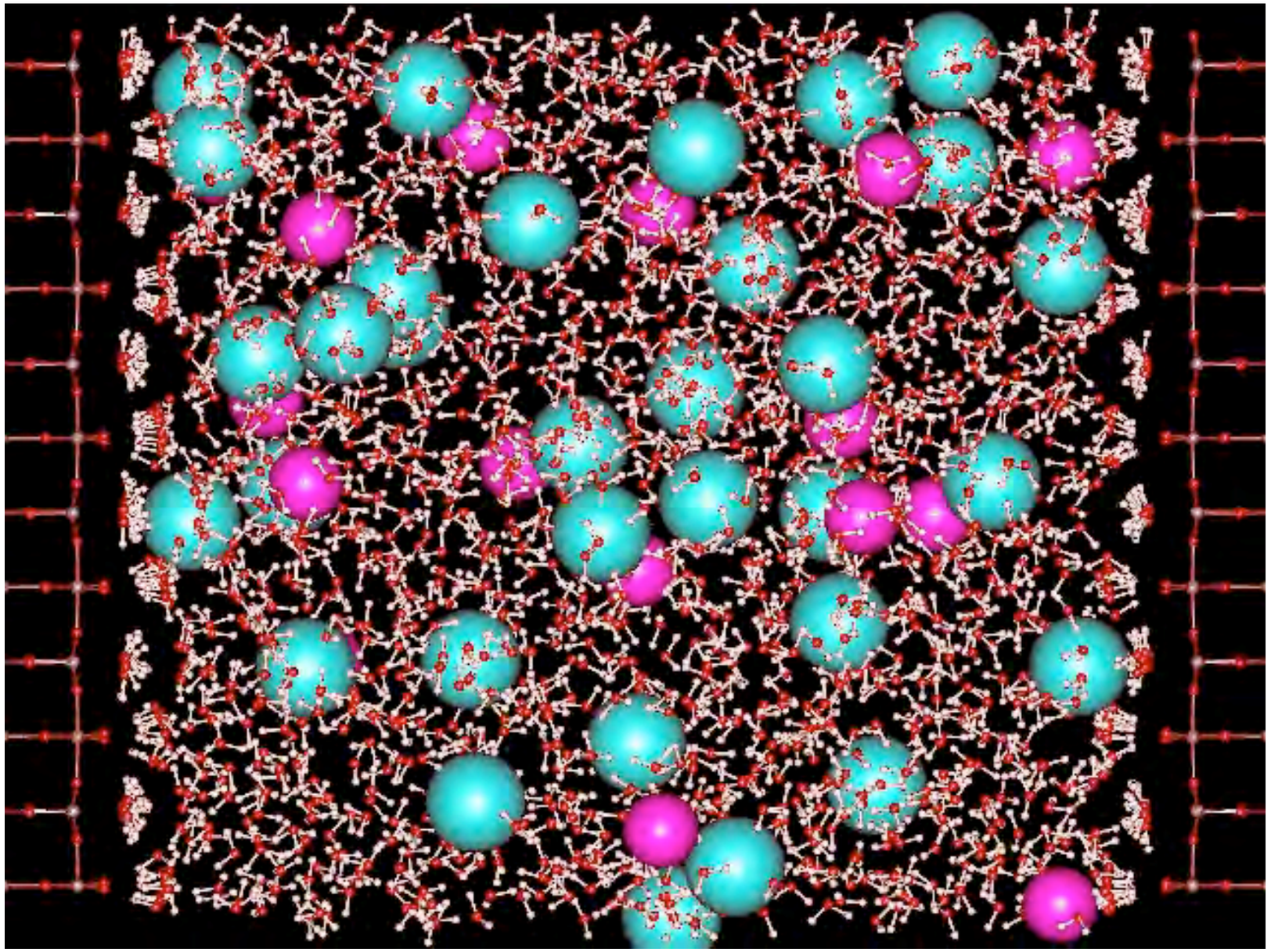
Molecular dynamics simulations

- Parallel periodic TiO_2 walls, 2 interfaces, wide slab
- L_x=39 Å, L_y =35.5 Å, $L_z \approx$ 50 Å



strontium

chloride

oxygen

titanium

hydrogen

Water molecules and surface atoms scaled down for clarity

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Model and potentials

- Rigid nonpolarizable model of water - SPC/E
- Structure and charges of TiO_2 surface - *ab initio* calculations
  - *Matsui and Akaogi potential for bulk TiO_2* (Mol. Sim. **6** (1991) 239)
  - *Relaxed structure with associatively or dissociatively adsorbed water molecules*
- Water-TiO_2 potentials
  - *$O(H_2)$-O(Ti) set to LJ potential of SPC water*
  - *$O(H_2)$-Ti refitted Fe^{3+}-$O(H_2)$ potential (force field optimization)*
  - *Coulombic interactions - partial charges (force field optimization)*
- Interaction potentials for ions
  - *Point charges + LJ potential*
    - *S. H. Lee and J. C. Rasaiah,* JPC ***100****, 1420 (1996)*
    - *B. J. Palmer, D. M. Pfund, and J. L. Fulton,* JPC ***100****, 13393 (1996)*

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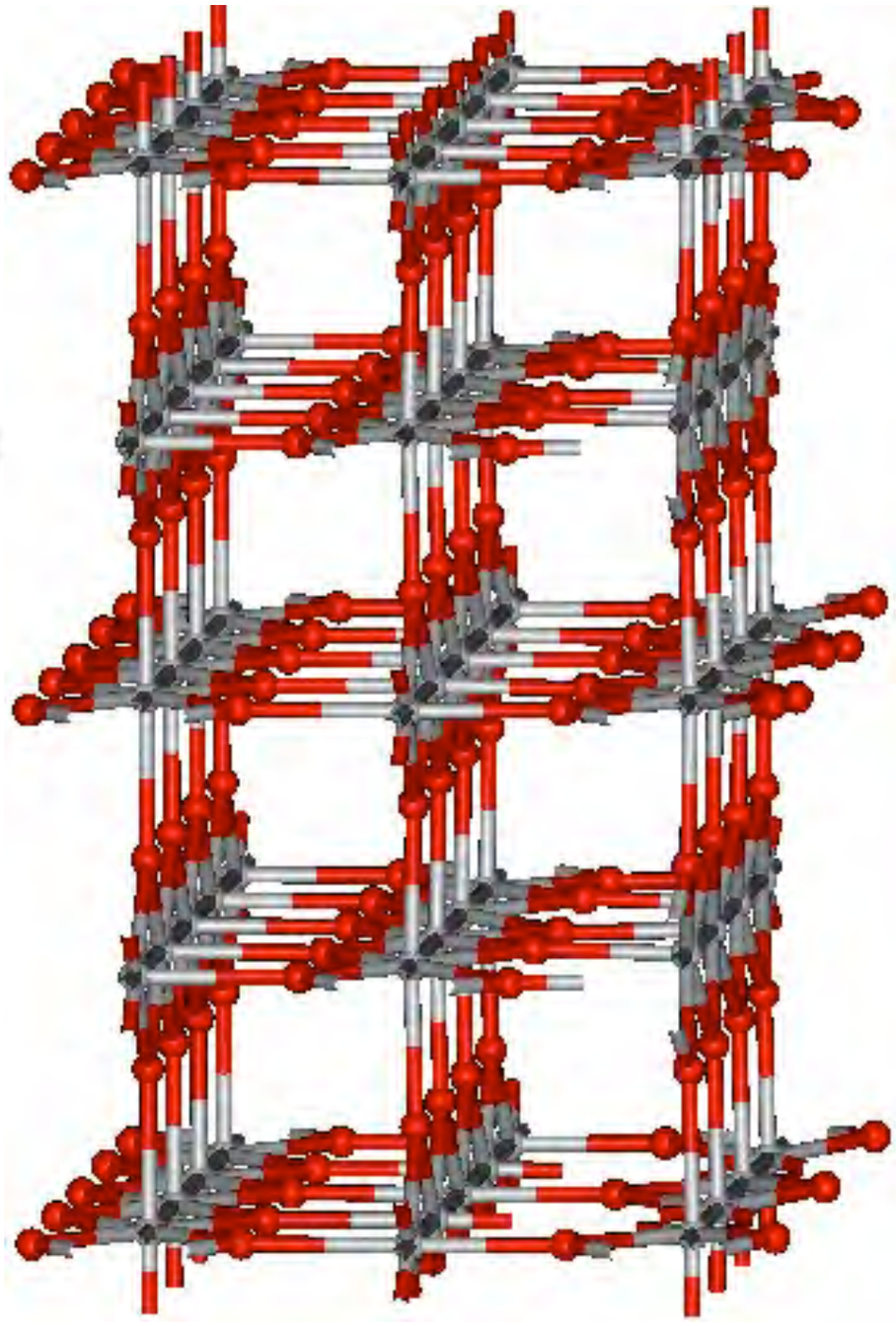
Nonhydroxylated surface

Hydroxylated

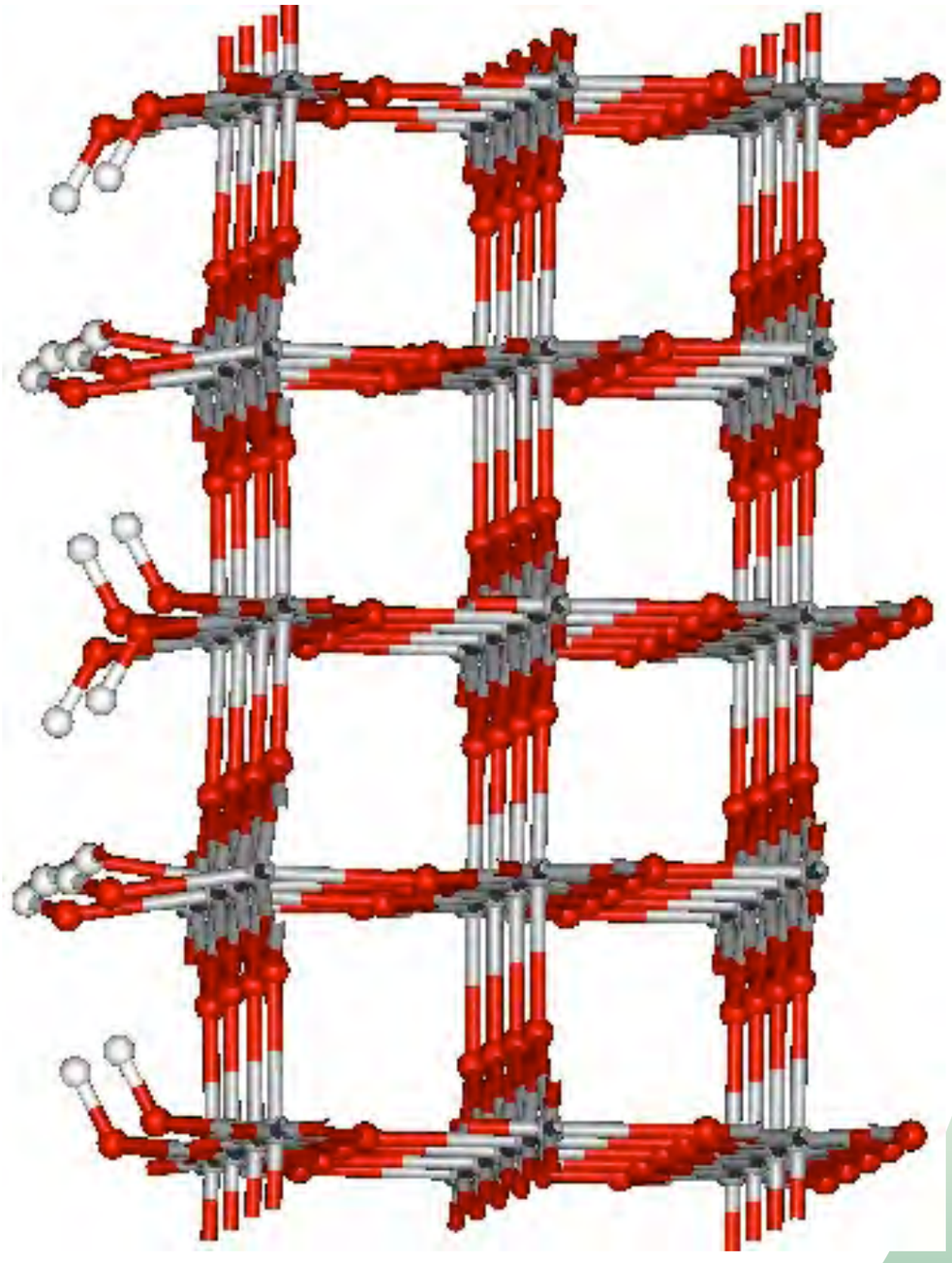
bulk TiO_2



bridging hydroxyl

terminal hydroxyl

aqueous solution



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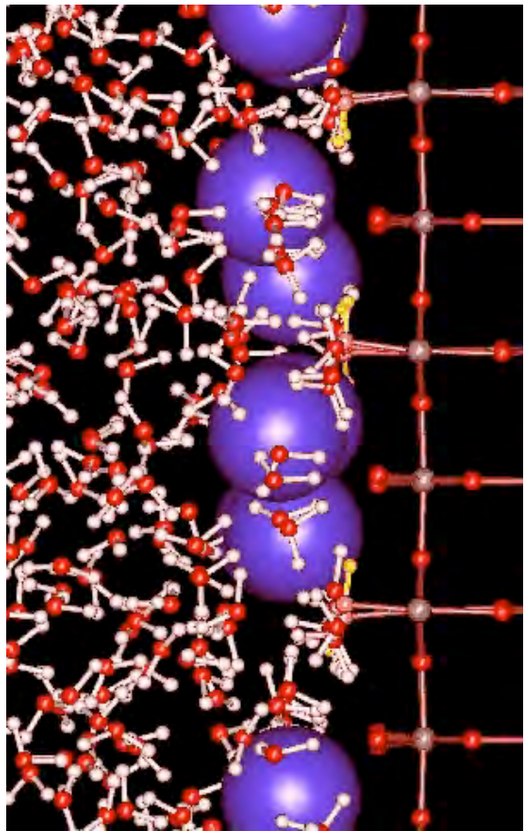
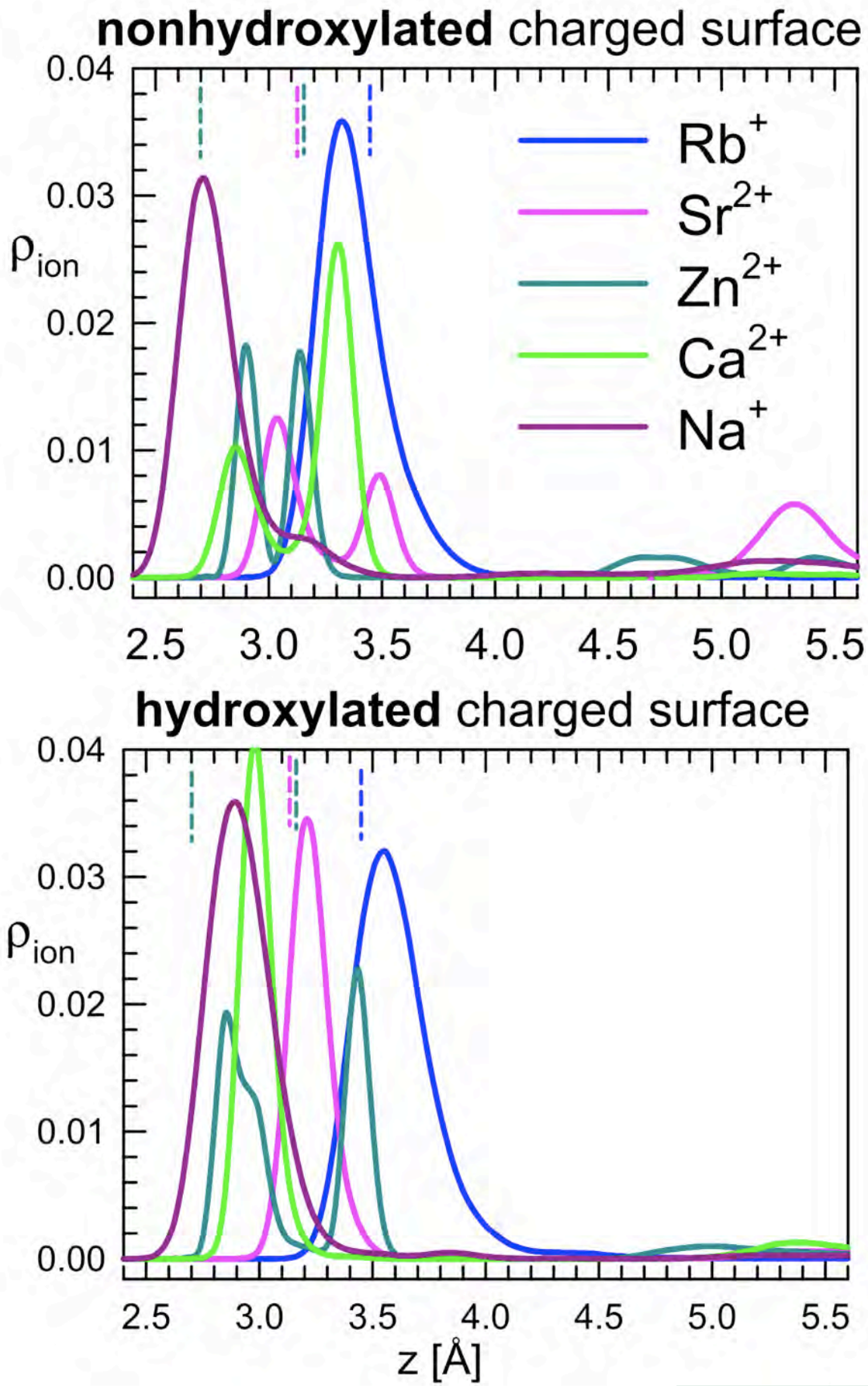
Axial density profiles of ions

- Comparison of MD results with XSW experimental data
- Better agreement for hydroxylated surface



Ion	Nonhydroxylated	Hydroxylated	X-ray
Rb^+	3.3	3.55	3.46
Sr^{2+}	3.0 3.5 5.3	3.2 5.7	3.13±0.04
Zn^{2+}	2.9 3.1	2.85 3.4	2.7±0.25 3.16±0.14
Ca^{2+}	2.85	3.0	—
Na^+	2.7	2.9	—



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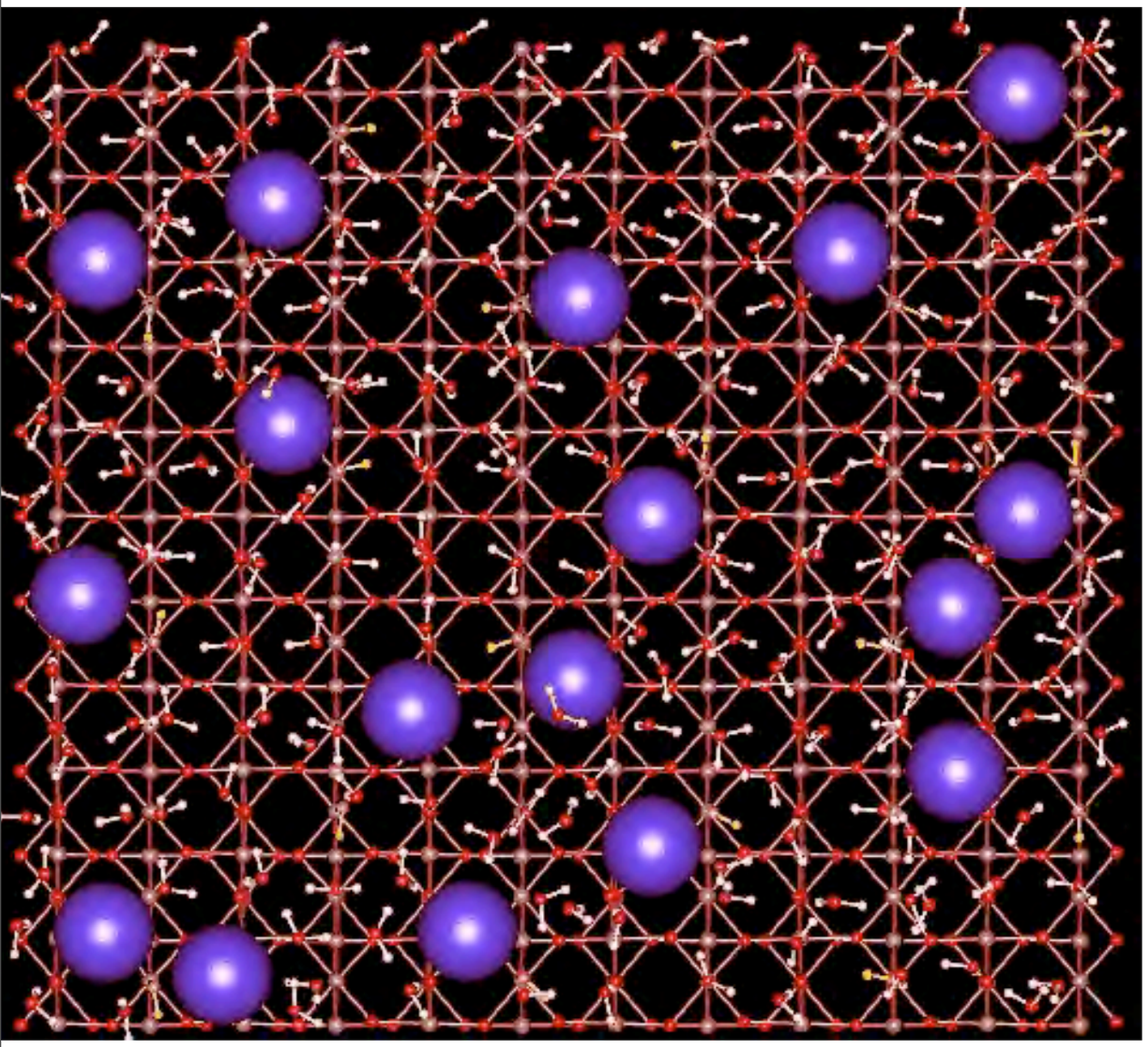
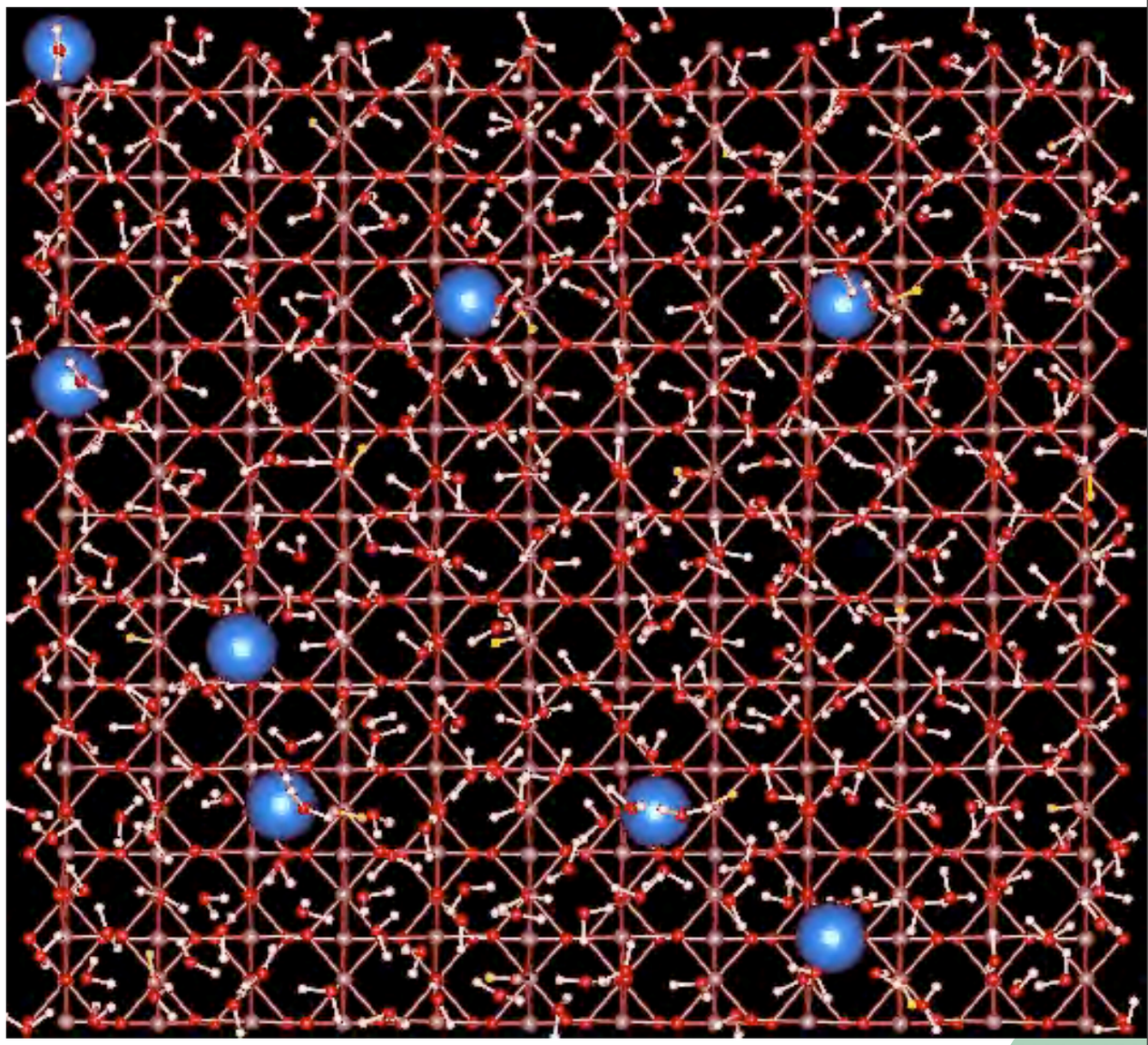
Lateral alignment of ions at charged surface

- rubidium



- zinc



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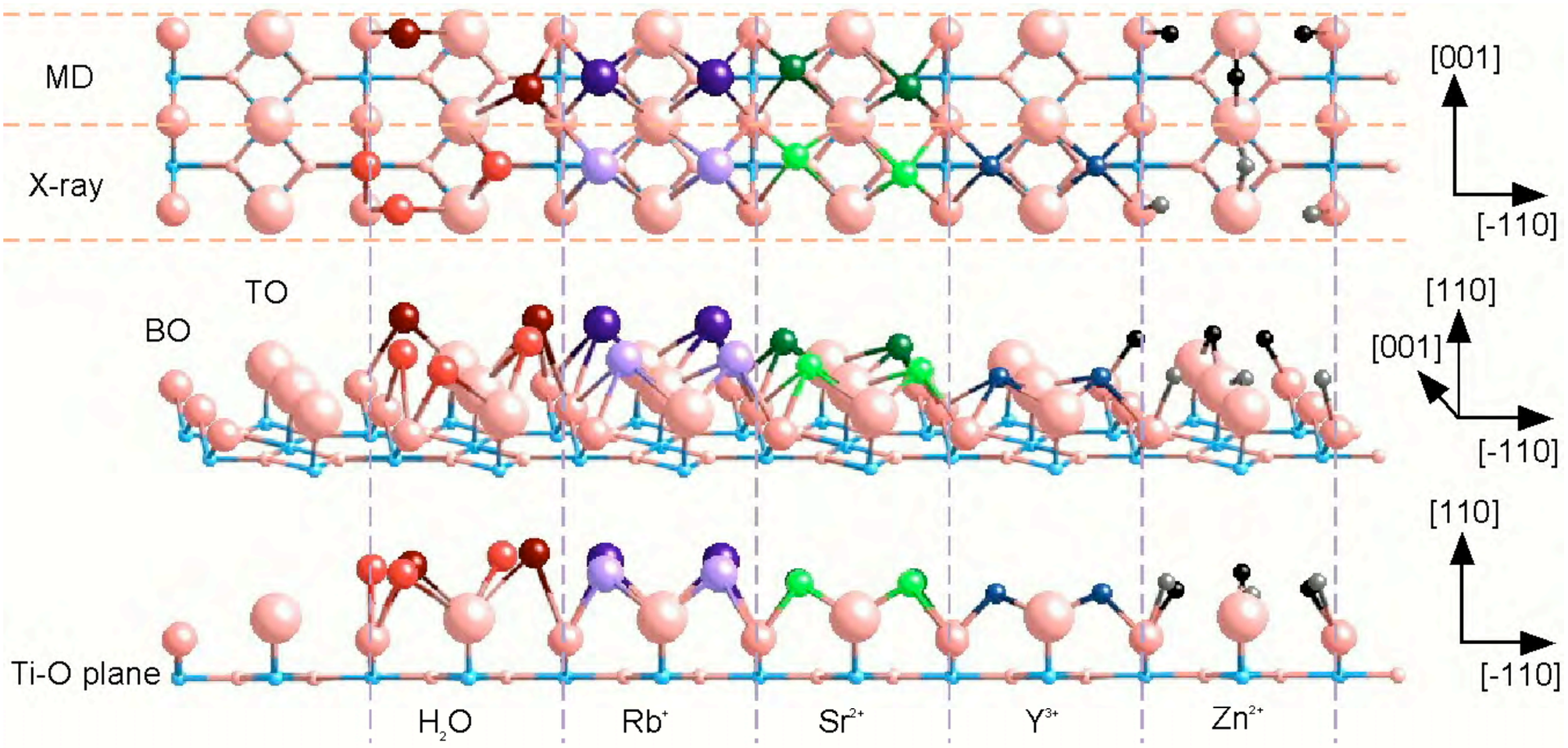
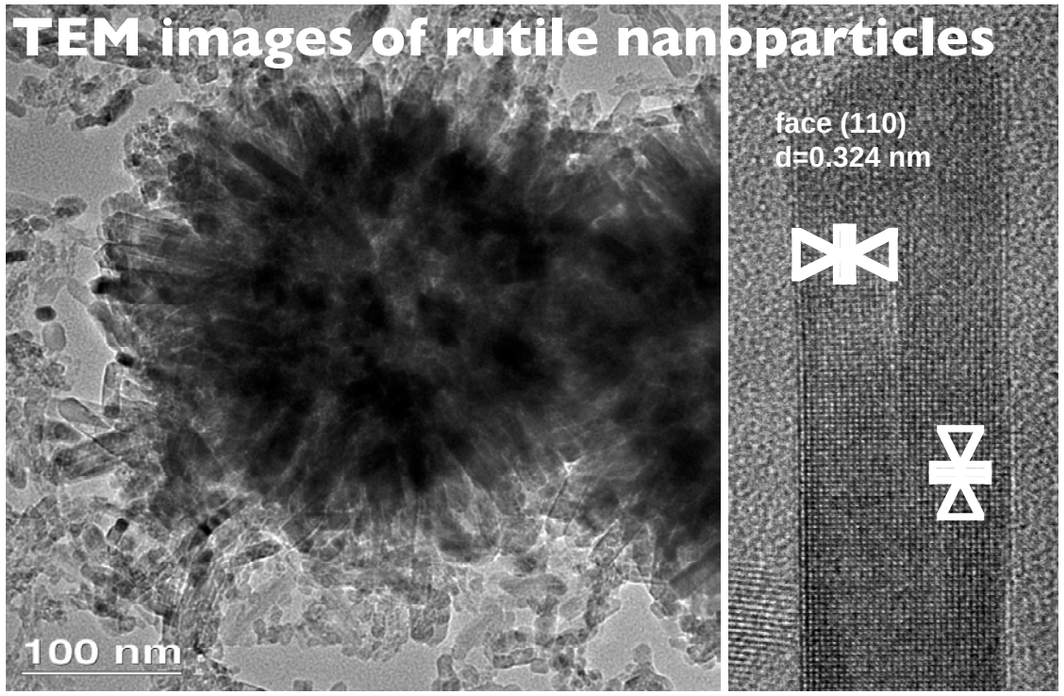
Key Result

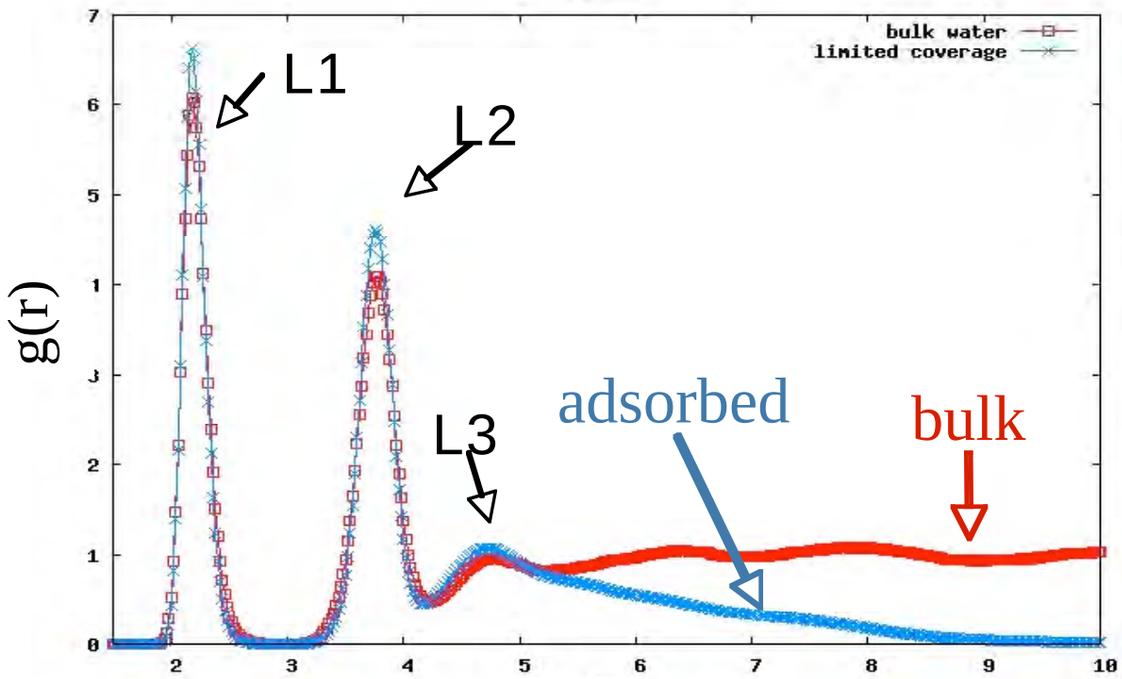
- Distribution of ions on surface (binding sites) and away from surface (density profiles)
  - *Zhang, Z., P. Fenter, L. Cheng, N.C. Sturchio, M.J. Bedzyk, M. Predota, A. Bandura, J. Kubicki, S.N. Lvov, P.T. Cummings, A.A. Chialvo, M.K. Ridley, P. Bénézeth, L. Anovitz, D.A. Palmer, M.L. Machesky and D.J. Wesolowski, Ion adsorption at the rutile-water interface: Linking molecular and macroscopic properties. Langmuir,* ***20*** *(2004) 4954-4969.*



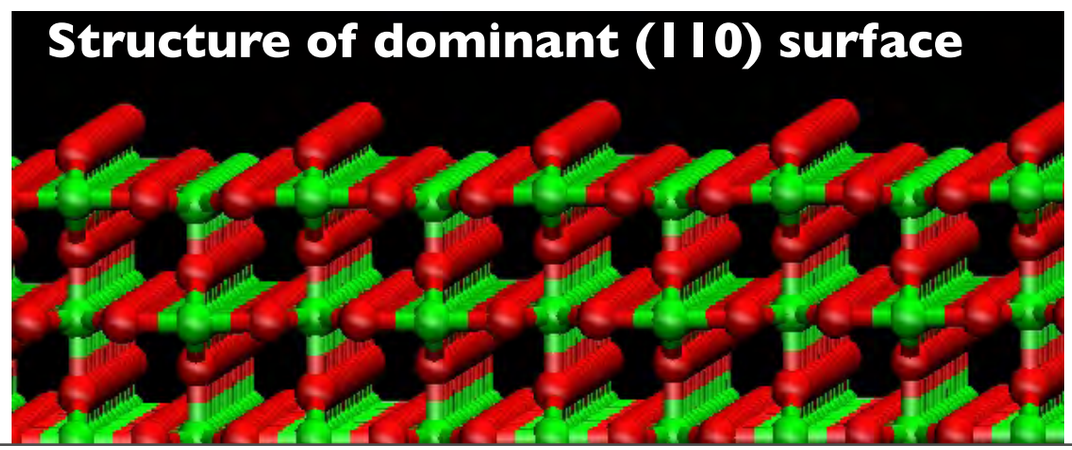
Water Adsorption at (110) Surface of Rutile (α-TiO_2)



MD density profiles of adsorbed water



- Thermal gravimetric analysis and mass spec experiments
  - *Determined the amount of adsorbed water.*
- Classical molecular dynamics simulations
  - *Water adsorbed from air forms three distinct layers*
    - Structure of the first two layers is the same as in the rutile/bulk water interface



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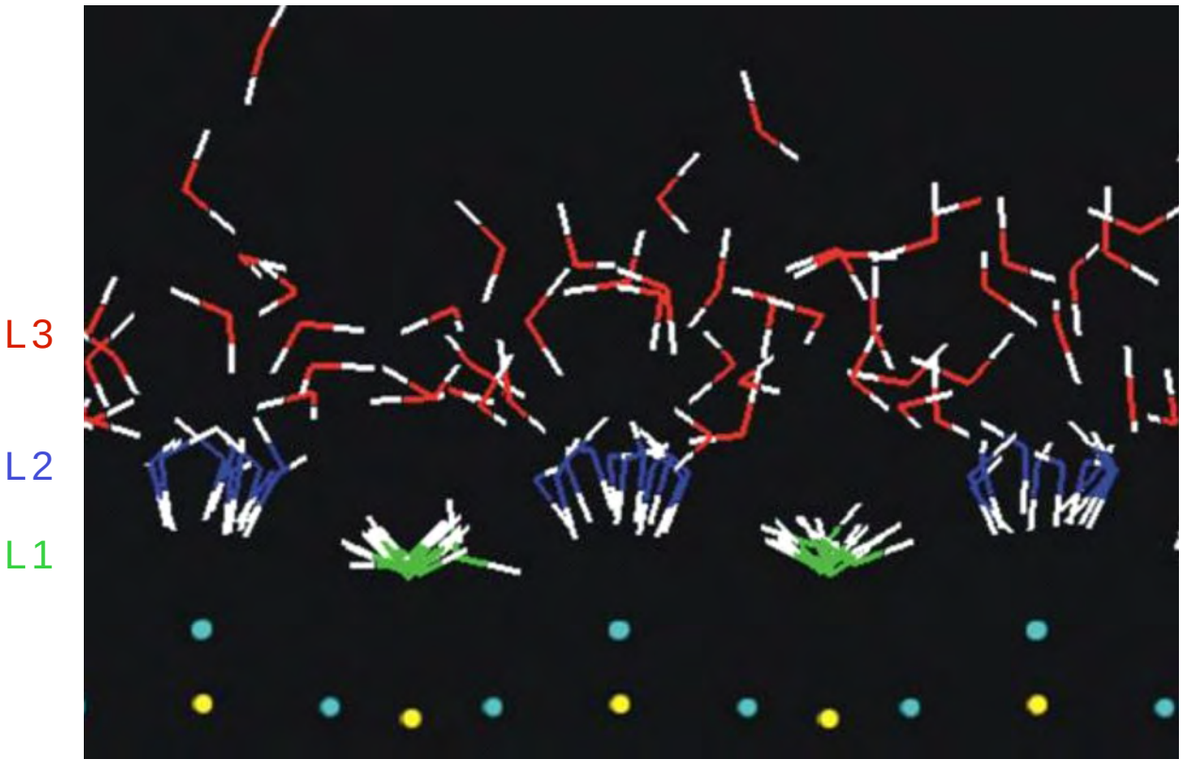
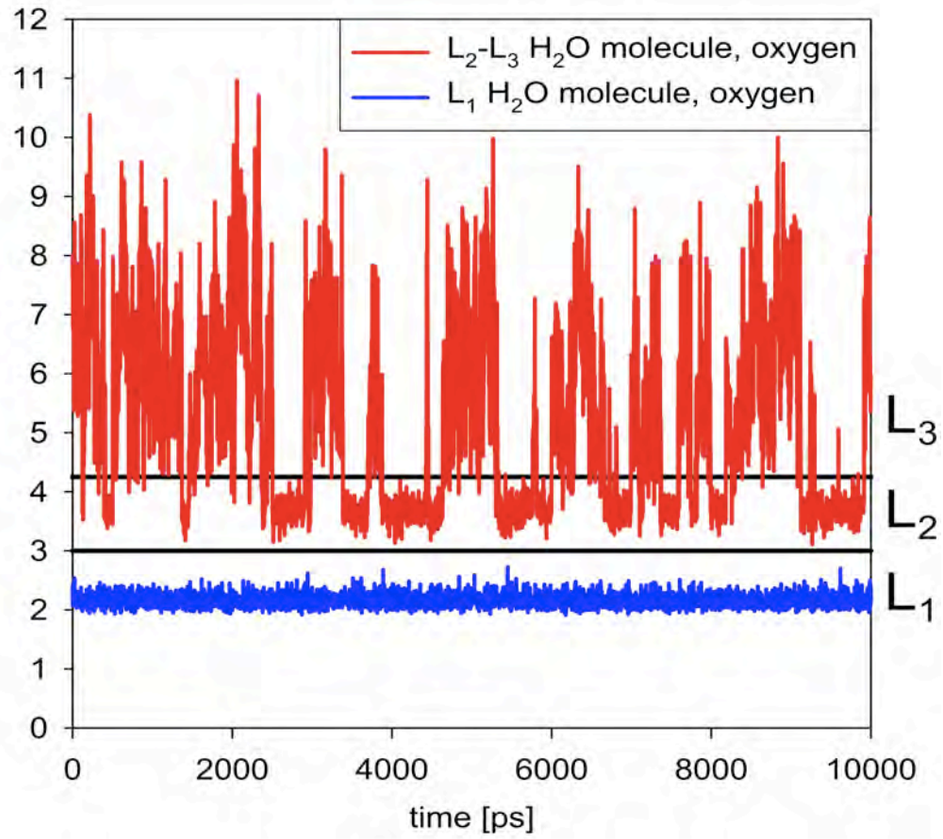
Comparing MD Simulations to QENS Experiments





Intermediate scattering function from trajectory

$$F(q,t) = \left\langle \frac{1}{N_p} \sum_{i=1}^{N_p} \exp\{i\mathbf{q}[\mathbf{r}_i(t) - \mathbf{r}_i(0)]\} \right\rangle$$

fit with →

$$F(t) = \exp\left[-(t/\tau)^{\beta}\right]$$

relaxation time

Dynamic structure factor from *F(q,t)*

$$S(q,\omega) = \frac{1}{\pi}\int_0^{\infty} \cos(\omega t) F(q,t)\, dt$$

fit with →

$$S(\omega) = \frac{1}{\pi}\frac{\Gamma}{\omega^2 + \Gamma^2}$$

$1/\tau$

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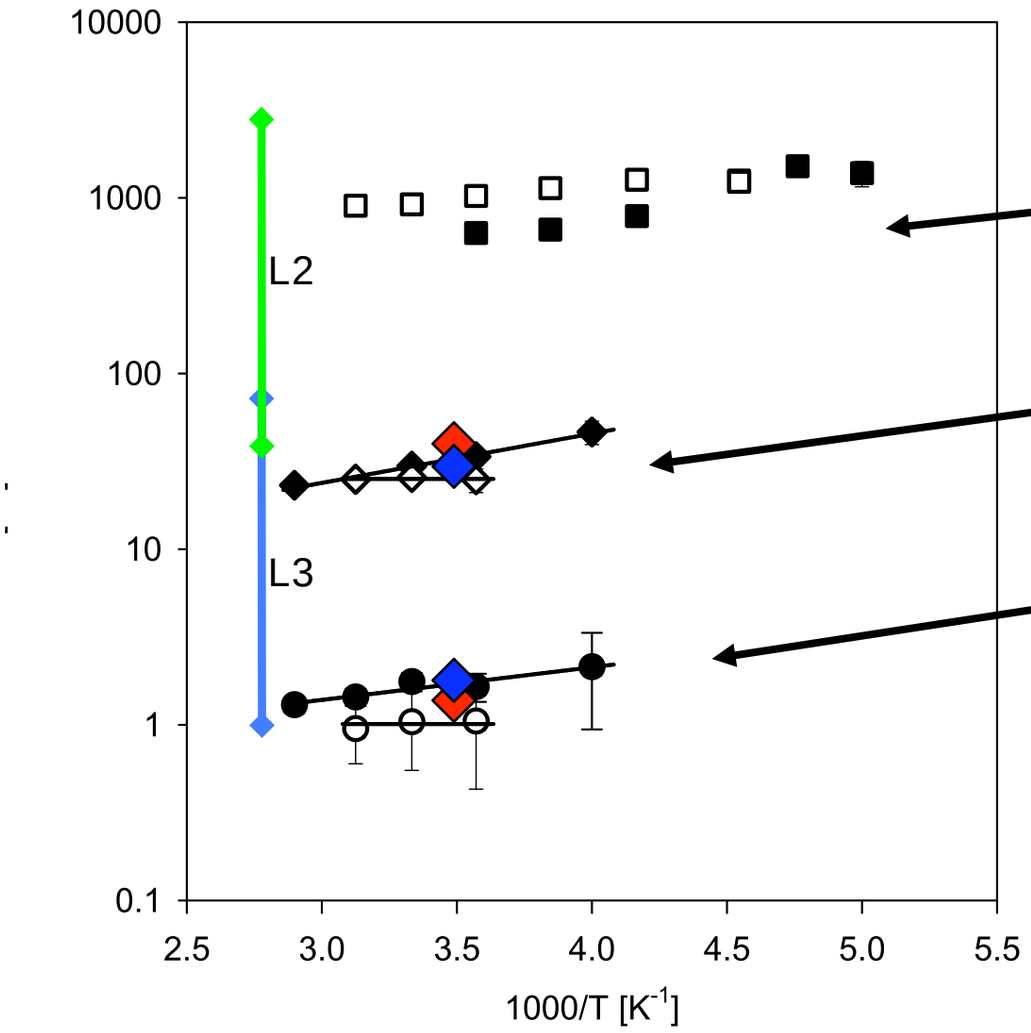
Proton Relaxation Times from QENS and MD

- Three layers of water at (α-TiO_2 and α-SnO_2)



Slow (HFBS) translational jumps between L2 and L3

Medium (DCS) translational within L3

– Fast (DCS) translation+rotation

DCS: Disc chopper time-of-flight spectrometer

HFBS: High flux backscattering spectrometer

Filled symbols – rutile (MD ◆)
Open symbols – cassiterite (MD ◆)

Mamontov, *et al. J. Phys. Chem. C* **111** (2007) 4328-4341
Mamontov, *et al. J. Phys. Chem. C* **112** (2008) 12334-12341
Mamontov, *et al. Phys. Rev. E.*, **79** (2009) Art. Num. 051504

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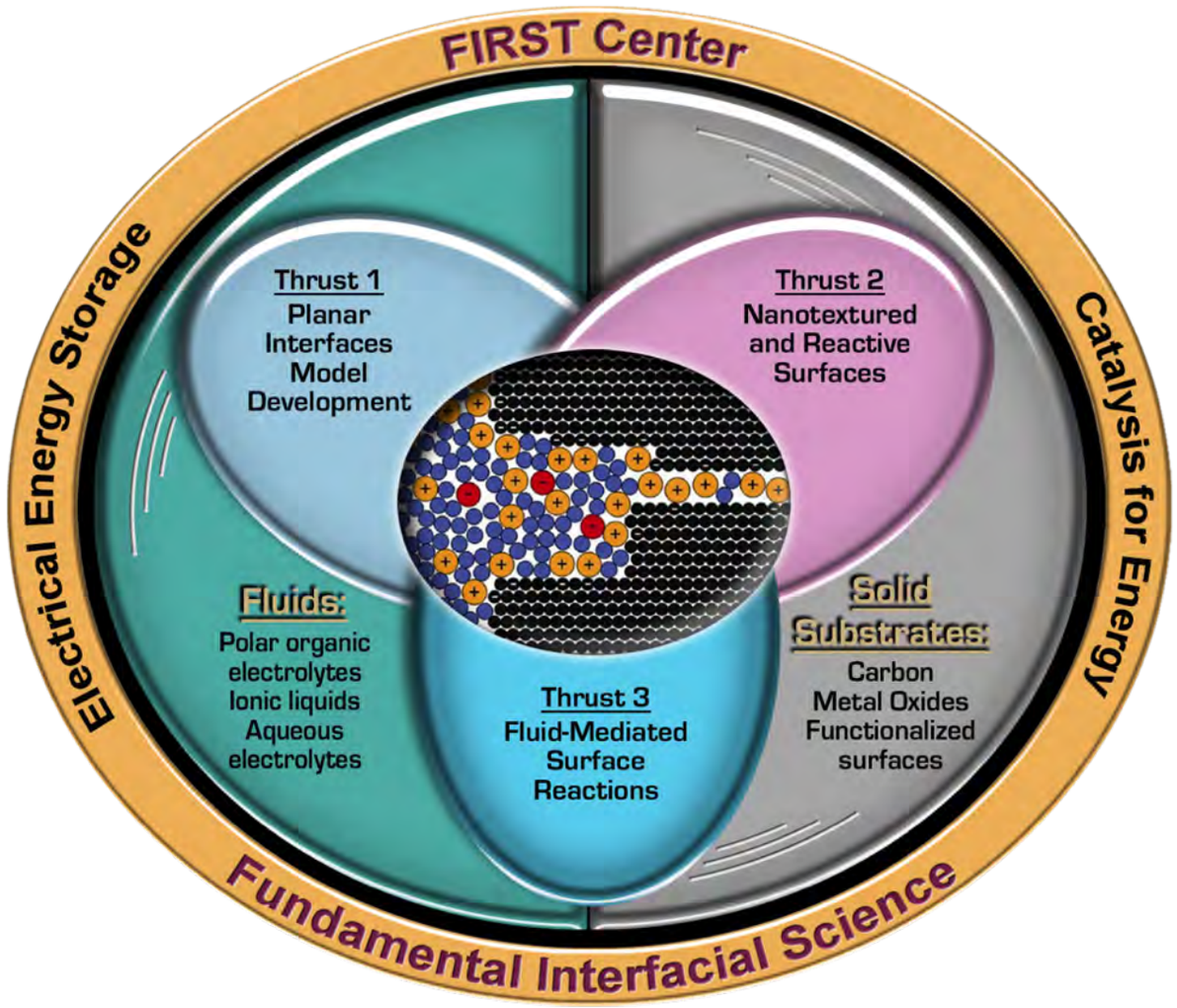
iTMSE

- We have named approach adopted in EDL project iTMSE
  - *Integrated theory, modeling, simulation and experiment*
- iTMSE is foundation for Fluid Interfaces: Structure, Reactions and Transport (FIRST) Engineering Frontier Research Center (EFRC)



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Role of TMS in Nanoscience

- Interpretation of complex phenomena in experiment
- Design of new nanostructured materials and systems based on *emergent phenomena* at nanoscale

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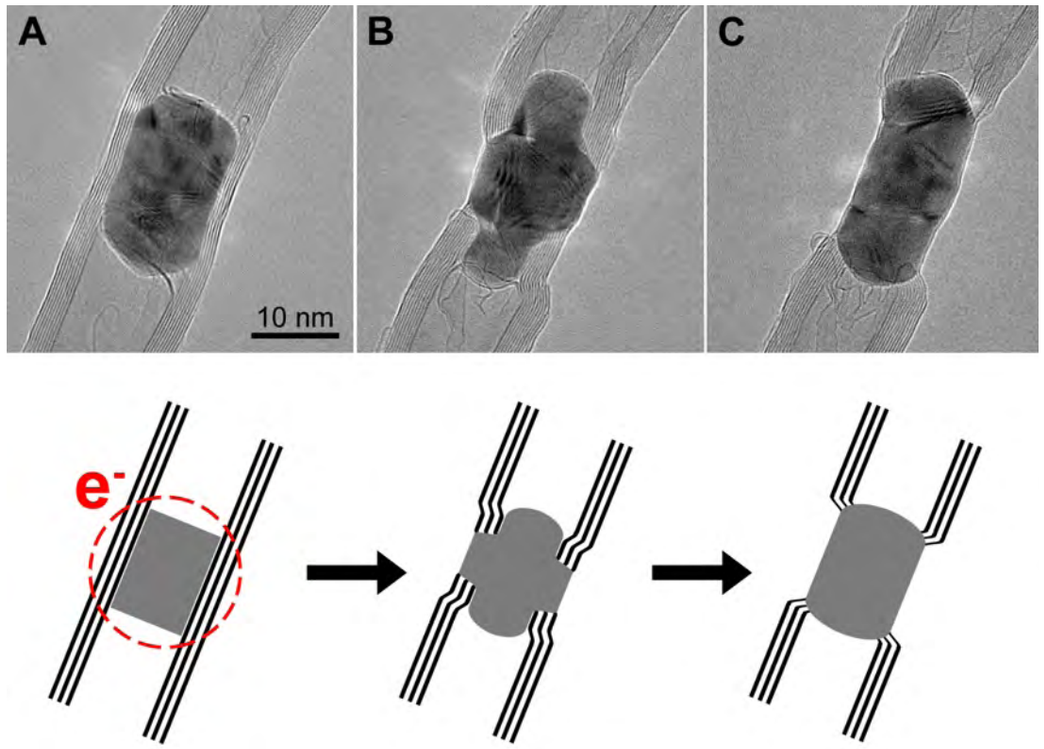
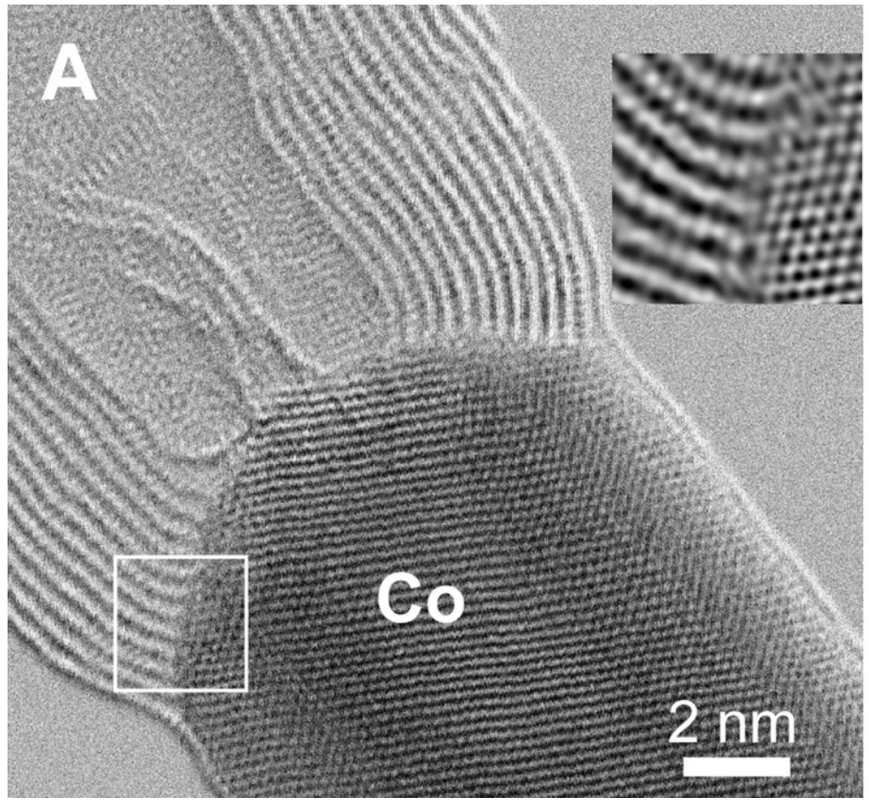
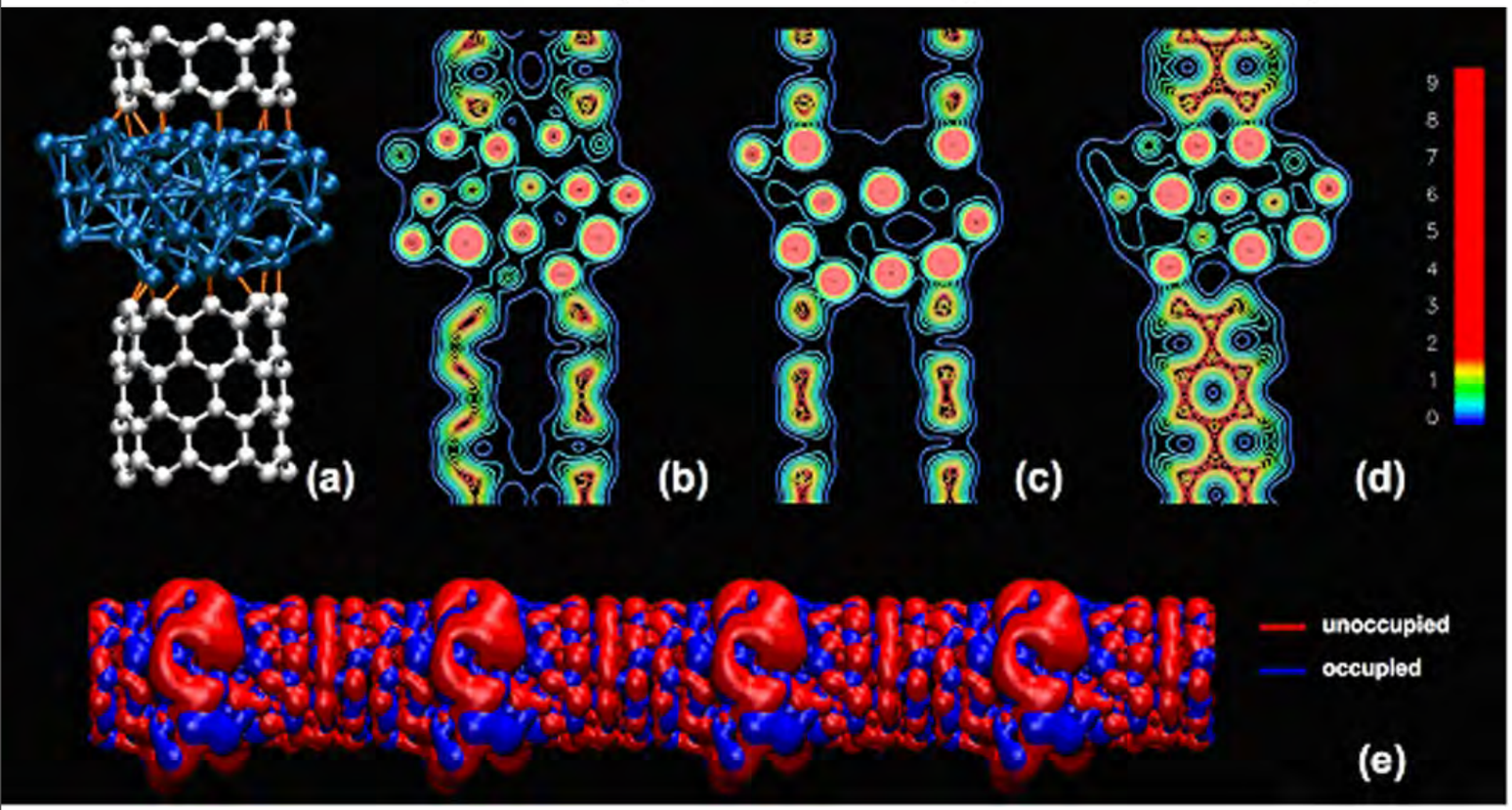
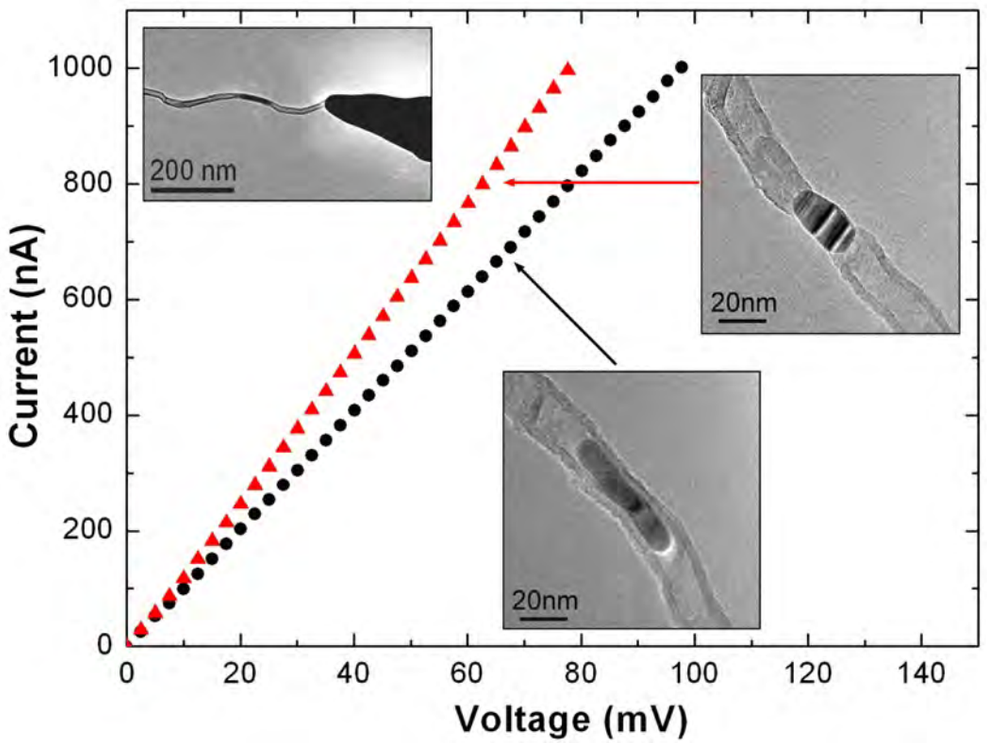
Structure and Electronic Properties at Nanoscale Heterojunctions

Heterojunctions are formed from metal-filled multi-wall carbon nanotubes (MWNTs) via intense electron beam irradiation at temperatures in the range of 450-700°C





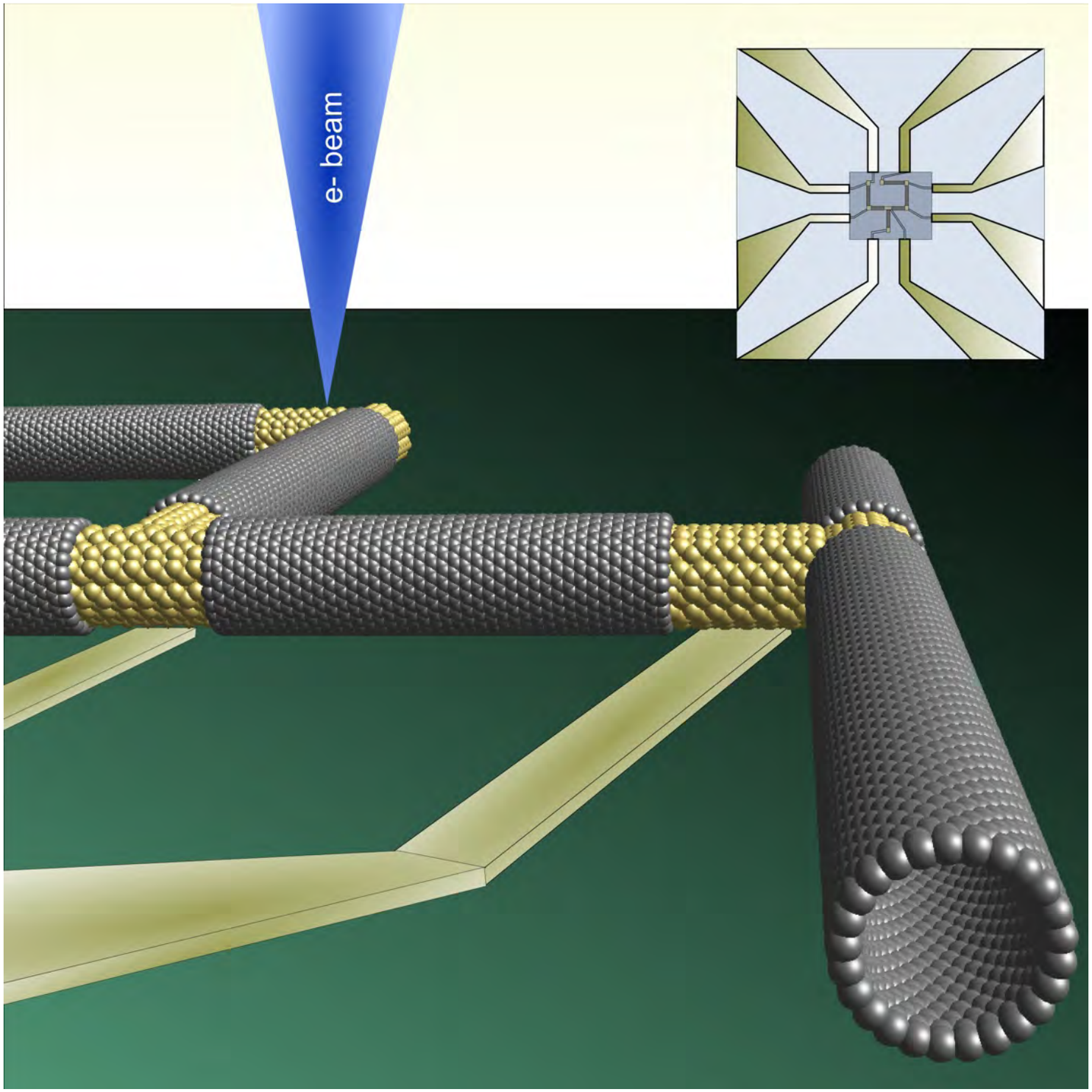




Covalent heterojunctions between carbon nanotubes and different metal nanocrystals (Fe, Co, Ni, and FeCo)

Rodriguez-Manzo, *et al.*, *Proc. Nat. Acad. Sci.* **106** (2009) 4591

Concept for E-Beam Processing Technique to Generate Ordered Networks of Nanotubes



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Role of TMS in Nanoscience

- Interpretation of complex phenomena in experiment
- Design of new nanostructured materials and systems based on *emergent phenomena* at nanoscale
- Fundamental insight into *emergent phenomena* at nanoscale
  - *Crucial to design manufacturing processes for nanostructured materials*
  - *Example - fluctuation theorems*

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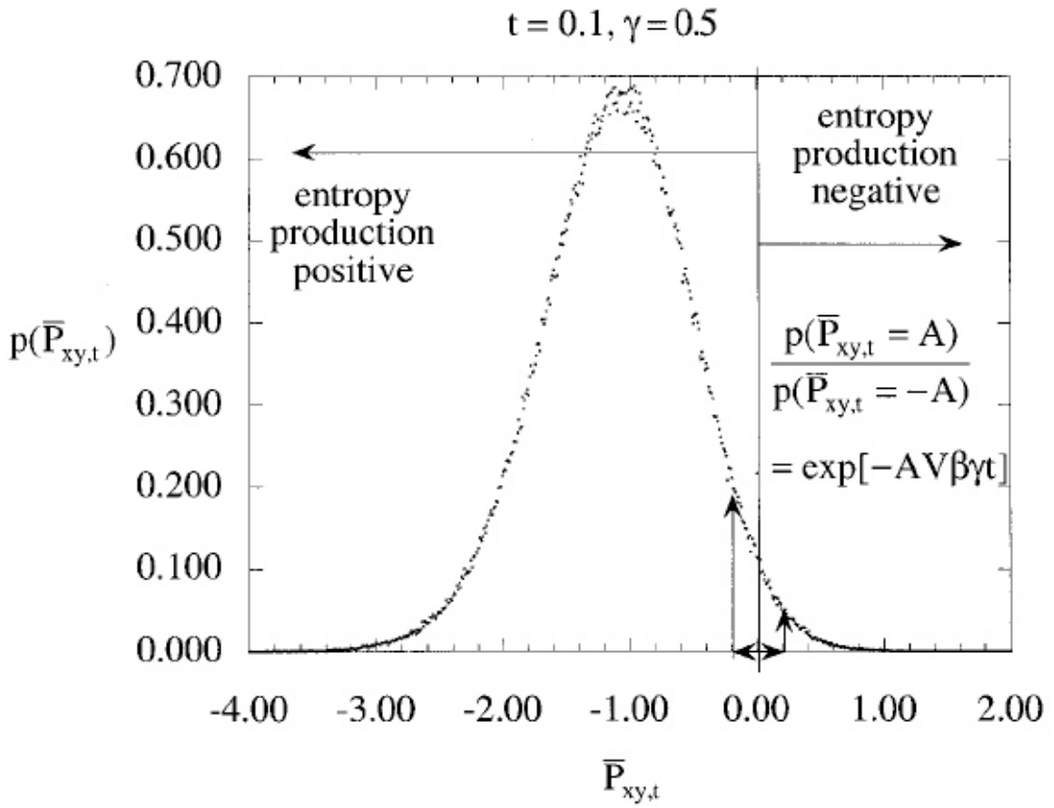
Theoretical Limits to Nanoscale Manipulation

- Recent theoretical development
  - *Evan's fluctuation theorem*
    - Quantifies the probability that a system will exhibit negative entropy production - NEP ("violate second law")
  - *Application to nanomachines*
    - There will be random (but with a defined mathematical frequency and length distribution) periods of NEP
      - *E.g., a nanomotor running backwards or manipulation resulting in atom moving in opposite direction of applied force*

$$\left[\frac{p(\bar{\Sigma}_t > 0)}{p(\bar{\Sigma}_t < 0)}\right] = \langle \exp(-\bar{\Sigma}_t t)\rangle_{\bar{\Sigma}_t<0} = \langle \exp(-\bar{\Sigma}_t t)\rangle^{-1}_{\bar{\Sigma}_t>0}$$

$\bar{\Sigma}_t$ = time - averaged entropy production



ADVANCES IN PHYSICS, 2002, VOL. 51, NO. 7, 1529–1585

Taylor & Francis
Taylor & Francis Group

The Fluctuation Theorem

DENIS J. EVANS*
Research School of Chemistry, Australian National University, Canberra, ACT 0200 Australia

and DEBRA J. SEARLES
School of Science, Griffith University, Brisbane, Qld 4111 Australia

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Experimental Verification

- *Phys. Rev. Lett.*, **89**, 050601 (2002); **92**, 140601(2004)
  - *Manipulation of a colloidal particle by optical tweezers*

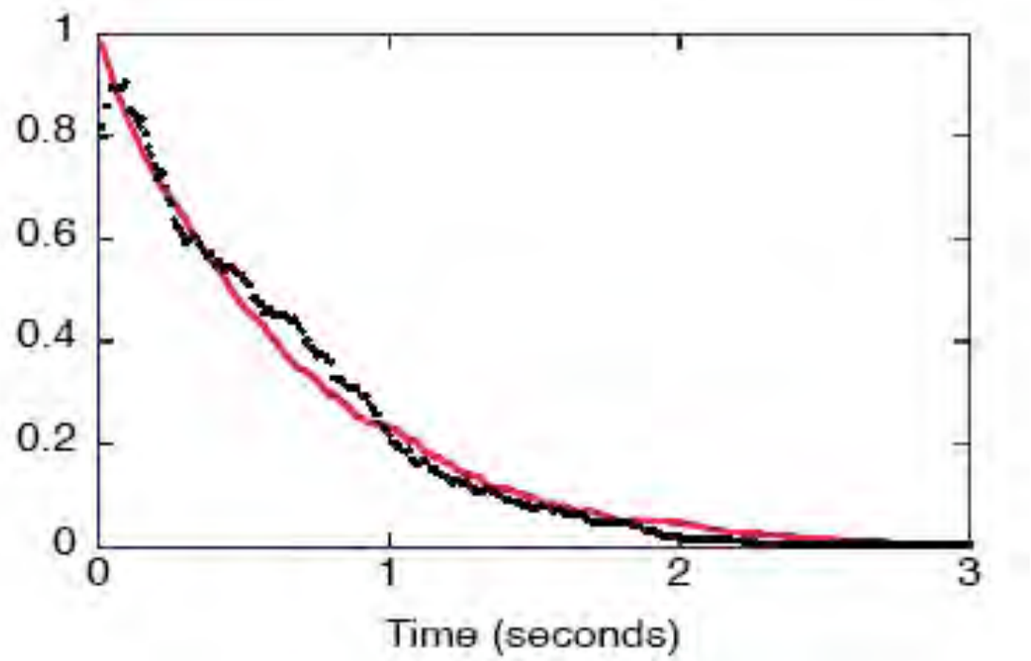

FIG. 2: The number ratio of entropy-consuming ($\Sigma_t < 0$) to entropy-producing ($\Sigma_t > 0$) trajectories (data points) and the entropy production averaged over entropy-producing trajectories, $\langle \exp -\Sigma_t \rangle_{\Sigma_t > 0}$ (grey line) versus duration, t, of 540 experimental trajectory, t. In accord with the IFT, both experimentally determined measures agree over time.

- *Additional verification: response of an electrical circuit to thermal noise*
  - Garnier and Ciliberto, Phys Rev. E, **71**, 060101 (2005)
- *Example of computational discovery*
  - Control of boundary conditions enabled isolation of phenomena

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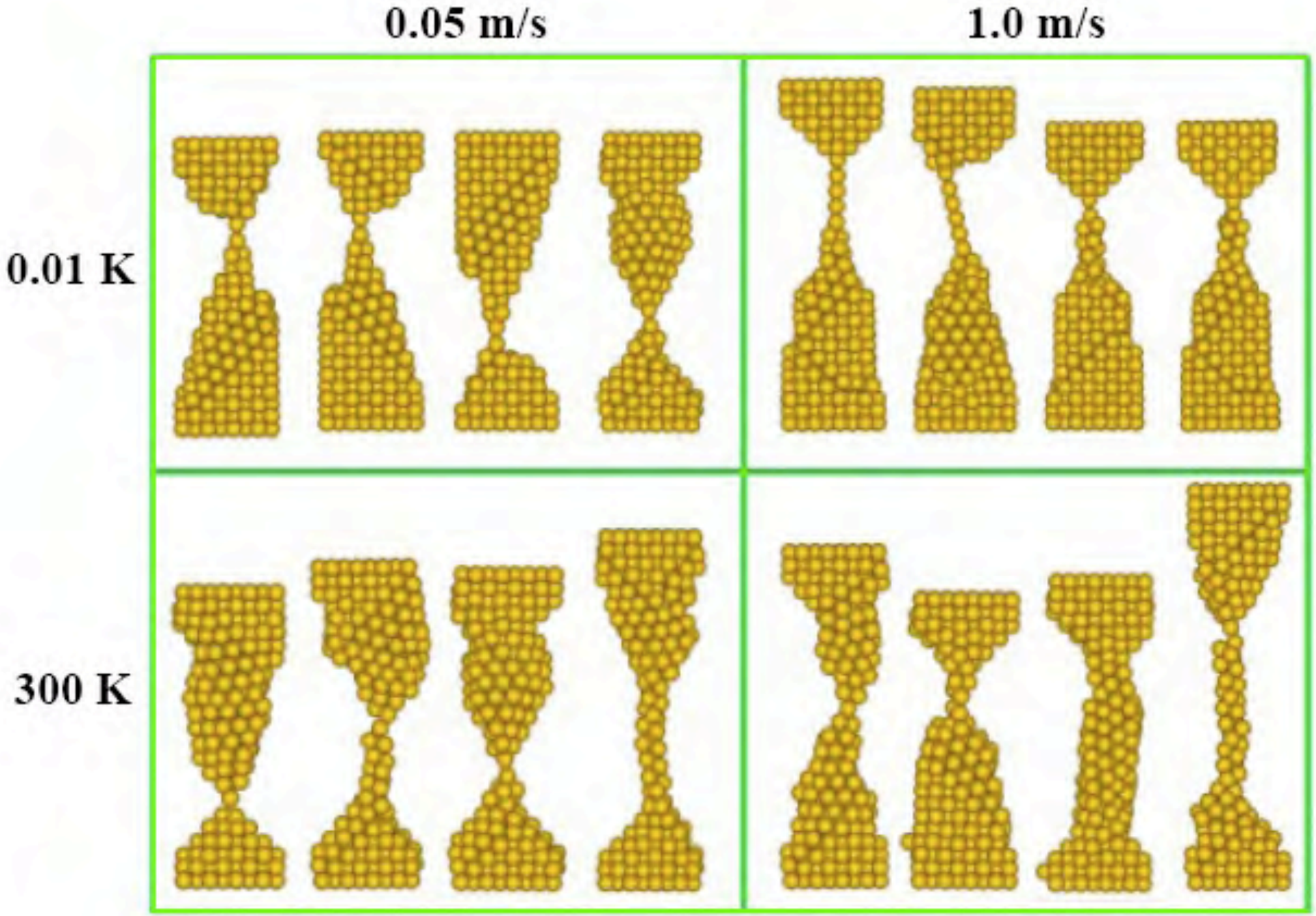
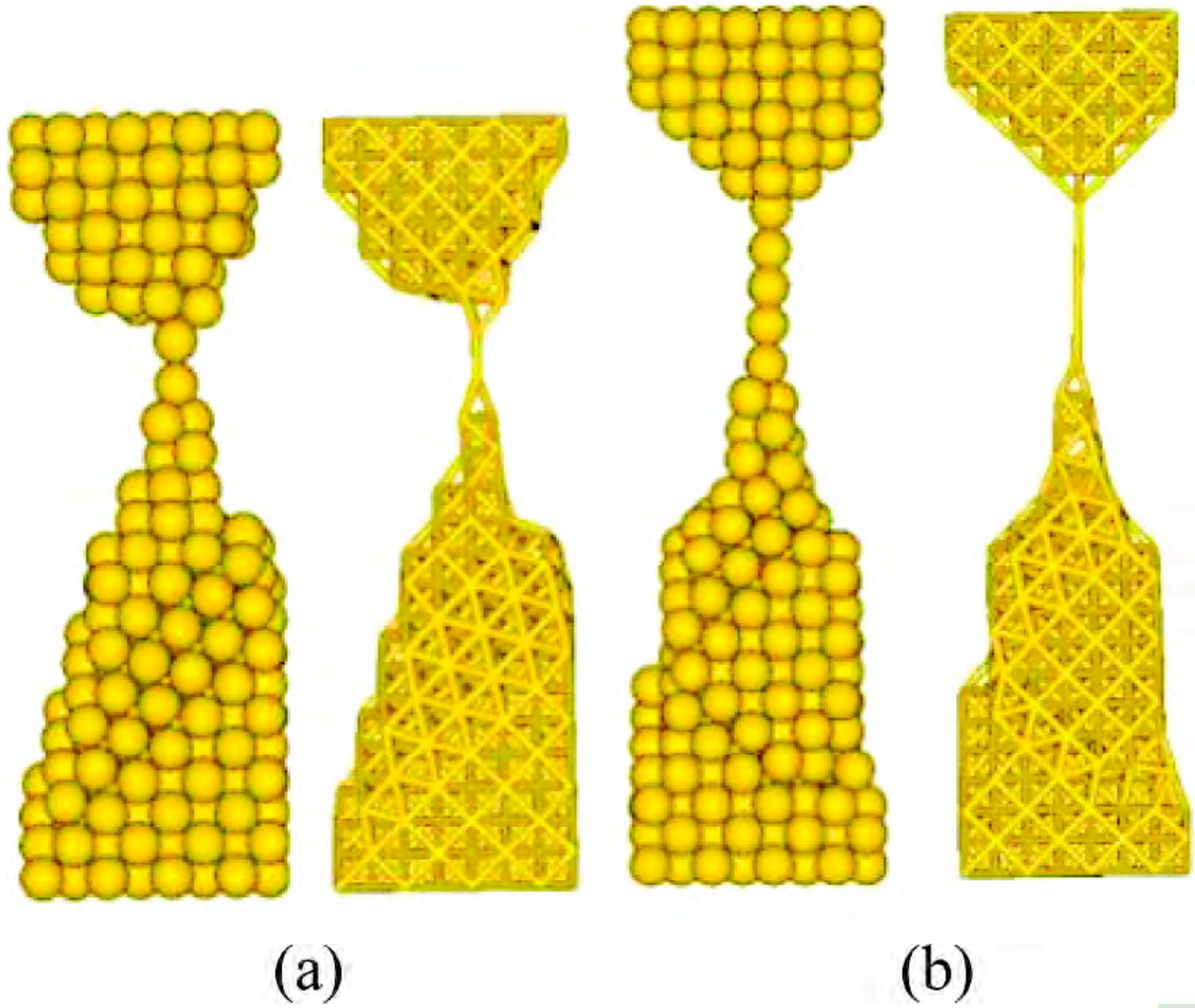
Unified Energy Release Mechanism in Rupture of Au Nanowires



Due diligence on forcefields: Pu *et al.*, *J. Chem. Phys.* **126** (2007) Art. No. 144707

Unified Energy Release Mechanism in Rupture of Au Nanowires

- 256-atom monatomic chains formed at 0.01 K
  - *Elongation rates of (a) 0.05 and (b) 1.0 m/s*
  - *Formation of 2-atom short chain at 0.05 m/s is accompanied by (111) reconstructions of the original (100) facets and well-defined dislocation lines at boundary between (111) and (100) facets*
  - *Less (111) patches are formed when the elongation rate is increased to 1 m/s*



Pu, *et al.*, *J. Am. Chem. Soc.*, **130** (2008), 17907

Conclusions

- Theory, modeling and simulation (TMS) play vital roles in nanoscale science and engineering
  - *Interpretation of experiments*
  - *Design of experiments*
  - *Characterization and design of nanostructured materials*
  - *Design and control of manufacture*
- TMS in nanoscale science and engineering
  - *Typically requires many different techniques*
  - *Future advances in field will result from development of additional methods*
    - Multiscale methods, electron transport dynamics, optical properties, self-validating forcefields,…
- Real advances in computational nanoscience need strong computational science/nanoscience integration
  - *Our experience has shown that the dividends paid far outweigh investment*

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