Quantum Simulations of Materials and Nanostructures

Giulia Galli

University of California, Davis

Collaborators: Z.Bai, F.Gygi and W.Pickett, UCD; W. Cai, Stanford U.; D.Ceperley, UIUC; N.Marzari, MIT; N.Spaldin, UCSB; E.Schwegler and J.-L.Fattebert, LLNL.

ASCAC Meeting, Nov. 6th, 2007

Quantum Simulations of Materials and Nanostructures (Q-SIMAN)

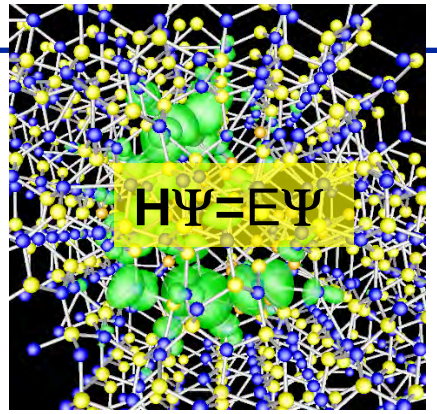
Predict and design molecular and materials properties with controllable accuracy, from first principles.

AREAS		GOALS
	Accuracy → Coupled AIMD/QMC techniques, including description of realistic environments	
	Robustness → Algorithms and codes for data analysis and validation	
	Efficiency → Linear scaling techniques and codes	
	and	
	Software → Specialized linear algebra; scalability and performance optimization for HPC and commodity clusters	

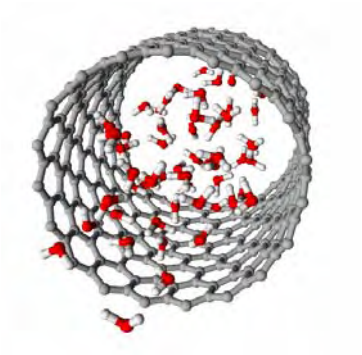
↓

Grand Challenge Applications to Materials and Nanostructures

Predictive modeling with controllable accuracy: a microscopic view in a nutshell



- We solve approximate form of the Schroedinger equation describing electron-electron and electron-ion interactions in molecules, condensed systems and nanostructures – no input from experiment.



- We couple our electronic structure description to statistical mechanical techniques to describe finite temperature properties and various thermodynamic conditions– *ab-initio* Molecular Dynamics; Monte Carlo

- We devise strategies and algorithms to compute 'complex' properties in realistic environments; this encompasses:

theoretical, algorithmic and software developments

Outline

- **Is computational materials science any good?** Any promising progress?
  - —A couple of examples
    - – Validation
    - – Impact

- Our strategy for predictive computations
  - —On different fronts, in parallel

- Some grand challenge applications

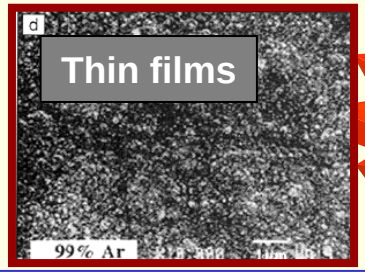
Terrestrial and extra-terrestrial ultra-disperse diamond

Extra-terrestrial diamond sources are often **ultra-disperse, with grain sizes of ~ 2-3 nm.**

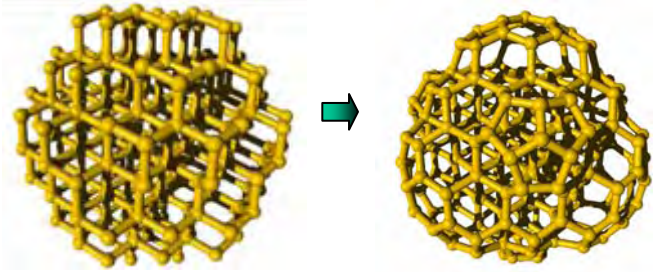
Why ?

Meteorite fragments

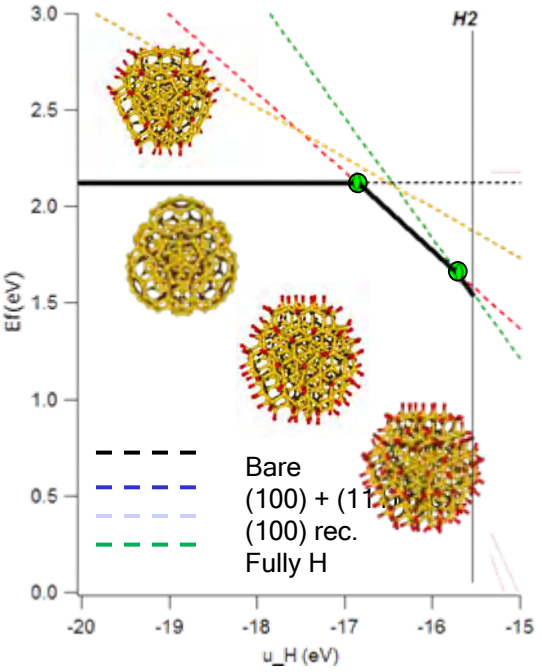
Some diamond films and detonation residues may also be ultra-disperse.



Detonation residues



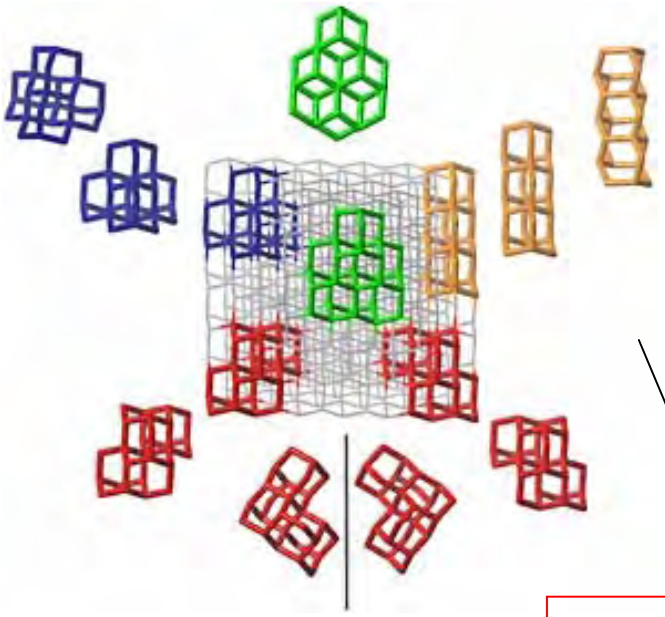
Model for bare nanodiamonds obtained by ab-initio MD (J.Y.Raty, G.Galli, A.Van Buuren and L.Terminello, PRL 03)



***Ab-initio* calculations** of formation energies of nanodiamond as a function of hydrogen content explain **enhanced stability of bare nanodiamonds in 2-3 nm range**, and diamond ultradispersity at the nanoscale.

(J.Y.Raty, G.Galli, Nature Materials 2003)

Hydrogenated diamond clusters (diamondoids) found in oil

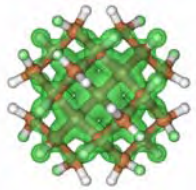


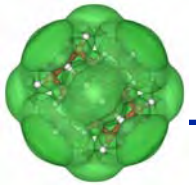
Functionalization (thiol groups) and deposition on Au and Ag surfaces

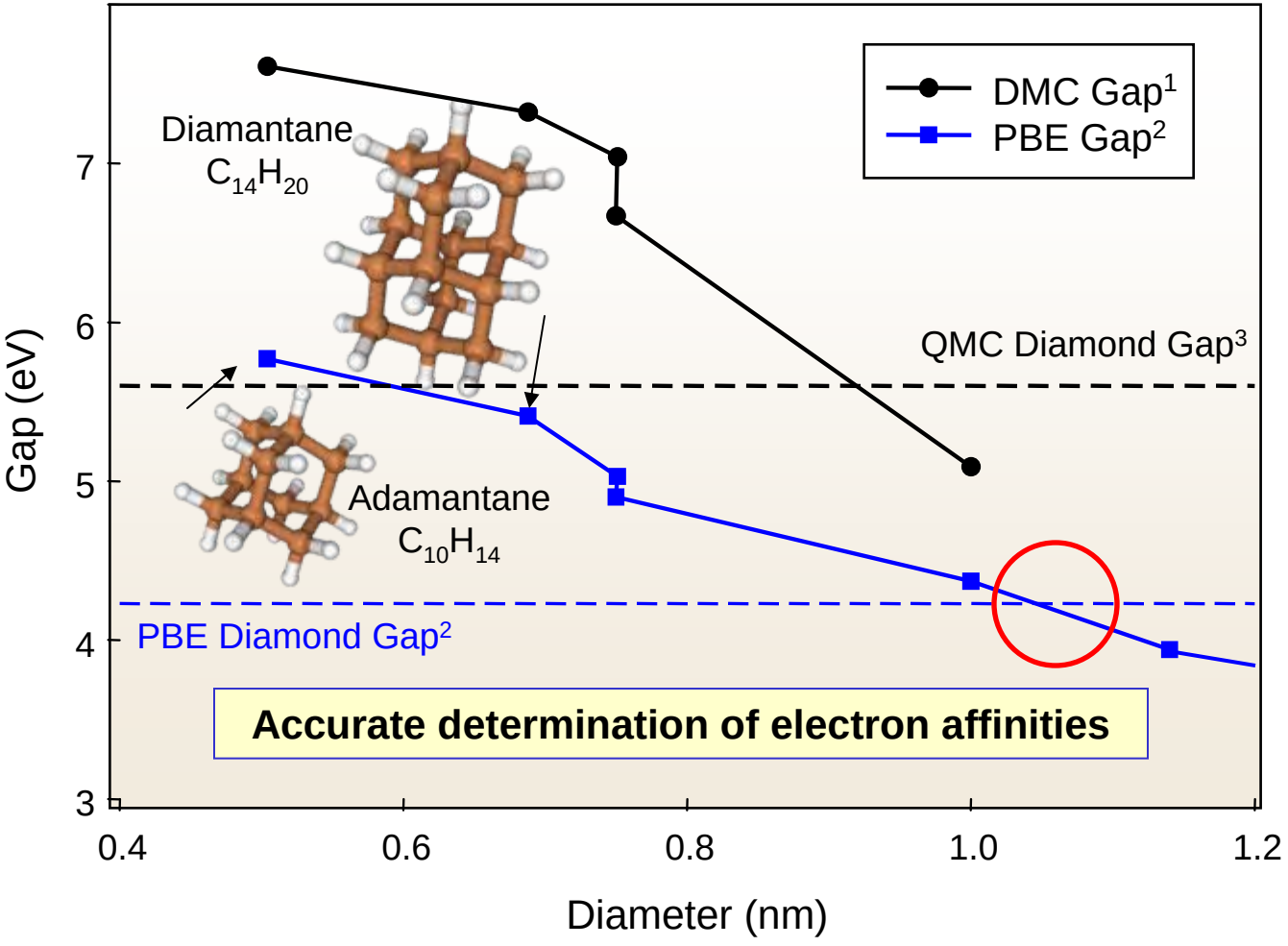
Chevron-Stanford project, 2006-

STM images of tetramantane: M.Crommie et al. (UCB,COINS)

Optical properties of diamondoids







Prediction: small diamondoids have negative electron affinity → electron emitters

Confirmed by experiments: Shen's group, Stanford, Science, 2007

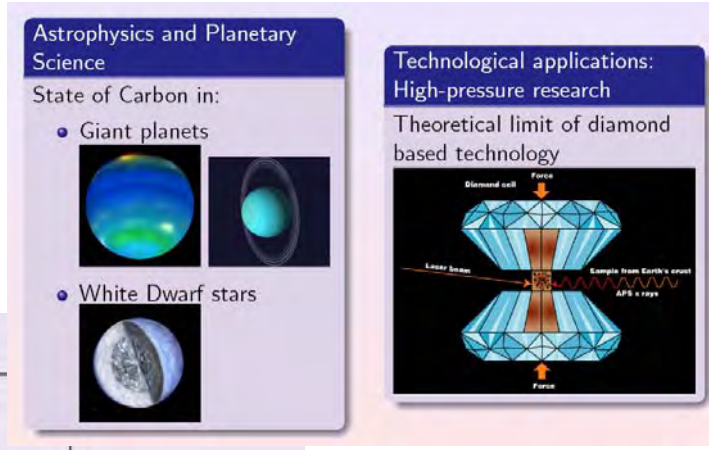
[1] N. Drummond, A.Williamson, R.Needs and G.Galli, PRL 2005

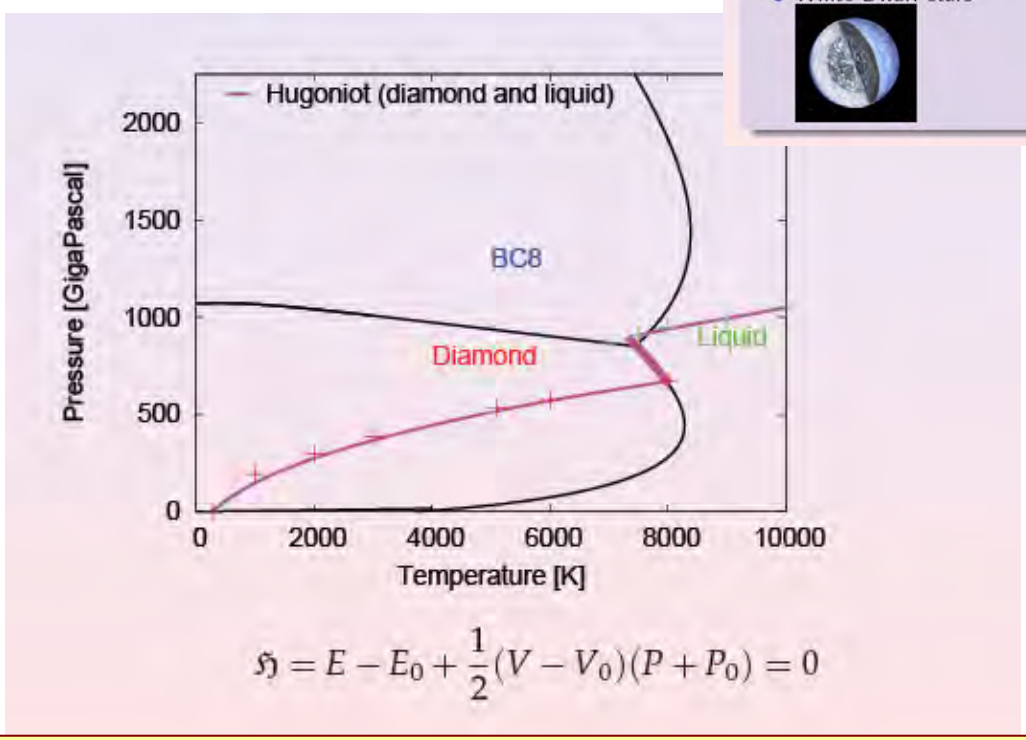
[2] J.-Y. Raty, G. Galli, C. Bostedt,T. W. van Buuren, and L.J. Terminello, Phys. Rev. Lett., 90, 037401 (2003)

[3] M. Towler, R.Q. Hood and R.J. Needs, Phys. Rev. B, 62, 2330 (2000)

High pressure phase diagram of carbon predicted by *ab-initio* molecular dynamics

- Melting at high pressure
- Change in electronic and bonding properties upon melting

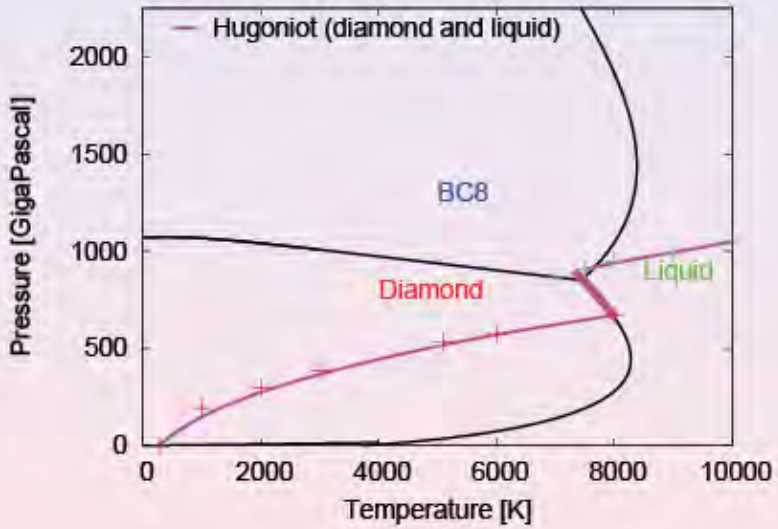




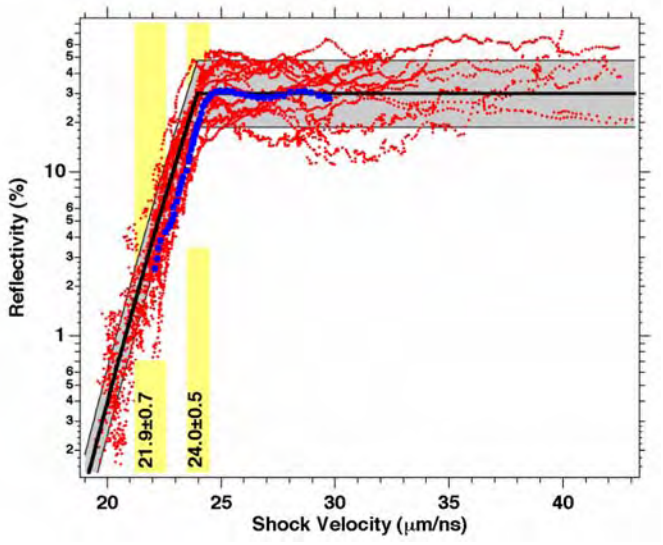
$$\mathfrak{H} = E - E_0 + \frac{1}{2}(V - V_0)(P + P_0) = 0$$

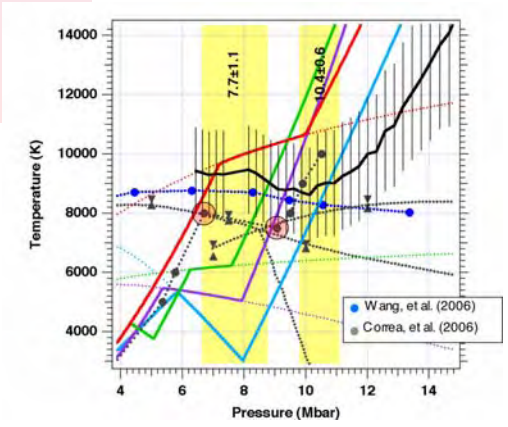
A.Correa, S.Bonev and G.G., PNAS 2006; in agreement with results from R. Car's group, PRL 2006

Recent shock experiments confirmed slope of diamond melting line and metallization upon melting



$$\mathfrak{H} = E - E_0 + \frac{1}{2}(V - V_0)(P + P_0) = 0$$

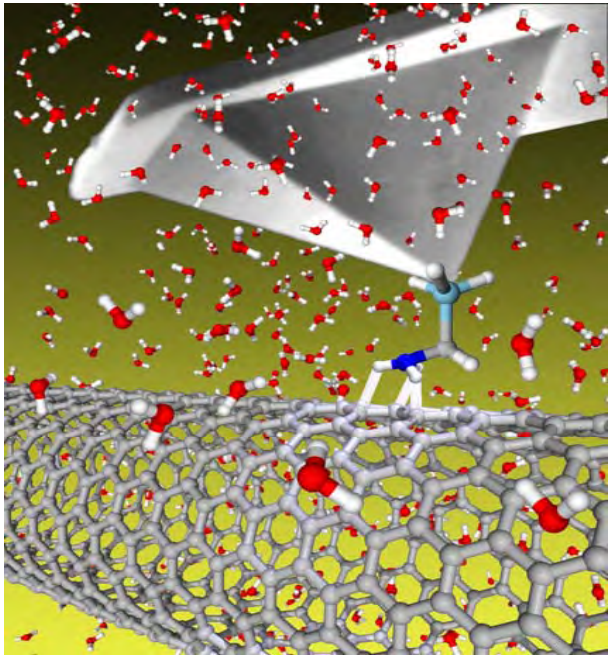




Ab-initio predictions used to interpret and guide current laser shock experiments

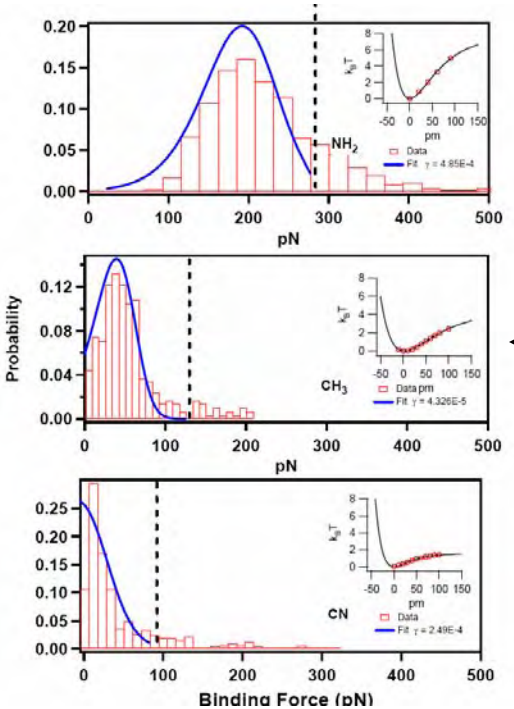
P.Loubyere et al. Nature Materials 2007

Single molecule interaction with Carbon Nanotubes



Nature Nanotec. 2007

Solvent effects on AFM measurements



Comparison with experiment in the presence of solvent

Theory helped interpret and design experiments

Outline

- **Is computational materials science any good?** **Any promising progress?**

  Yes!

  —A couple of examples

  - **Validation**
  - **Impact**

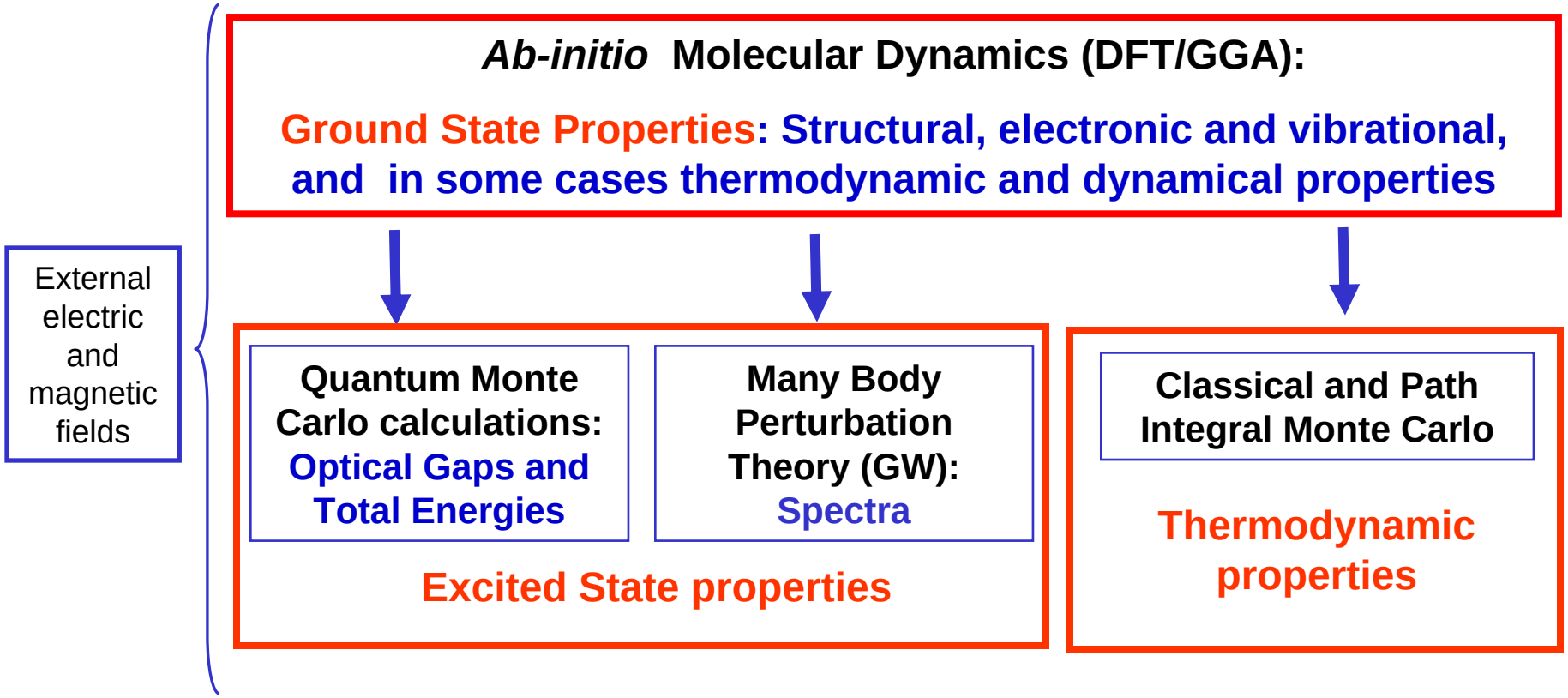
Outline

- Is computational materials science any good? Any promising progress?
  - —A couple of examples
    - – Validation
    - – Impact

- Our strategy for predictive computations
  - —On different fronts, in parallel

- Some grand challenge applications

Predictive modeling with controllable accuracy



Ab-initio Molecular Dynamics (DFT/GGA):

Ground State Properties: Structural, electronic and vibrational, and in some cases thermodynamic and dynamical properties

Solve set of N coupled, non linear partial differential equations self-consistently, using iterative algorithms, subject to orthonormality constraints. N = # of electrons

$$\begin{cases} -\Delta\varphi_i + V(\rho,\mathbf{r})\varphi_i = \varepsilon_i\varphi_i \quad i = 1\ldots N_{\text{el}} \\ V(\rho,\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) + \int \dfrac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + V_{\text{XC}}(\rho(\mathbf{r}),\nabla\rho(\mathbf{r})) \\ \rho(\mathbf{r}) = \sum_{i=1}^{N_{\text{el}}} |\varphi_i(\mathbf{r})|^2 \\ \int \varphi_i^*(\mathbf{r})\,\varphi_j(\mathbf{r})\,d\mathbf{r} = \delta_{ij} \end{cases}$$

Plane-wave basis sets and pseudopotentials

The cost of solving the Kohn-Sham equations is eventually dominated by orthogonalization (O(N^3))

Ab-initio Molecular Dynamics (DFT/GGA):

Ground State Properties: Structural, electronic and vibrational, and in some cases thermodynamic and dynamical properties

Optimization of 10^6 to 10^9 degrees of freedom for 10^4 to 10^6 time steps

$$\begin{cases} -\Delta\varphi_i + V(\rho,\mathbf{r})\varphi_i = \varepsilon_i\varphi_i \quad i = 1\ldots N_{\text{el}} \\ V(\rho,\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) + \int \dfrac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + V_{\text{XC}}(\rho(\mathbf{r}),\nabla\rho(\mathbf{r})) \\ \rho(\mathbf{r}) = \sum_{i=1}^{N_{\text{el}}} |\varphi_i(\mathbf{r})|^2 \\ \int \varphi_i^*(\mathbf{r})\,\varphi_j(\mathbf{r})\,d\mathbf{r} = \delta_{ij} \end{cases}$$

Plane-wave basis sets and pseudopotentials

The cost of solving the Kohn-Sham equations is eventually dominated by orthogonalization (O(N^3))

Focus on optimized Kohn-Sham solvers, reduced scaling algorithms and data compression

Qbox

Petascale architectures

Optimization of 10^6 to 10^9 degrees of freedom for 10^4 to 10^6 time steps

$$\begin{cases} -\Delta\varphi_i + V(\rho,\mathbf{r})\varphi_i = \varepsilon_i\varphi_i \quad i = 1\ldots N_{\text{el}} \\ V(\rho,\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) + \int \dfrac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + V_{\text{XC}}(\rho(\mathbf{r}),\nabla\rho(\mathbf{r})) \\ \rho(\mathbf{r}) = \sum_{i=1}^{N_{\text{el}}} |\varphi_i(\mathbf{r})|^2 \\ \int \varphi_i^*(\mathbf{r})\,\varphi_j(\mathbf{r})\,d\mathbf{r} = \delta_{ij} \end{cases}$$

(*) Gordon-Bell Award 2006, F.Gygi et al.

Optimized Solvers: Z.Bai and F.Gygi; Reduced scaling algorithms: F.Gygi and J.-L.Fattebert; Data compression: F.Gygi

A Subspace Bisection Algorithm for Electronic Structure Data Compression

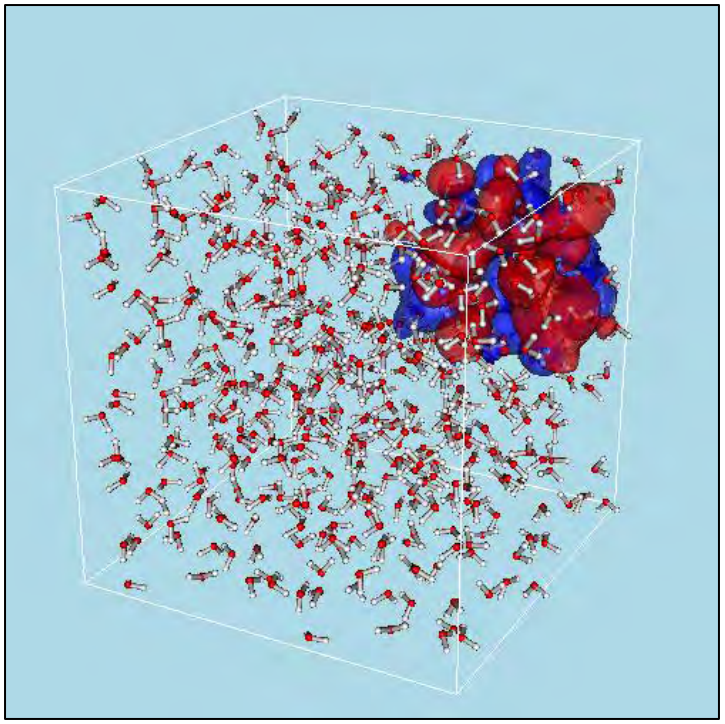
- The size of electronic structure data grows as $O(N^2)$
- Goal: Compressing electronic structure data while preserving accuracy
- A compression algorithm based on the CS decomposition was tested on $(H_2O)_{512}$ and a 304-atom CNT
- A compression ratio of 4.0 ($(H_2O)_{512}$) and 2.7 (CNT) can be achieved
- We are developing a recursive version of the algorithm to achieve higher compression ratios

The Subspace Bisection algorithm reduces I/O volume and restart file size on large-scale parallel platforms

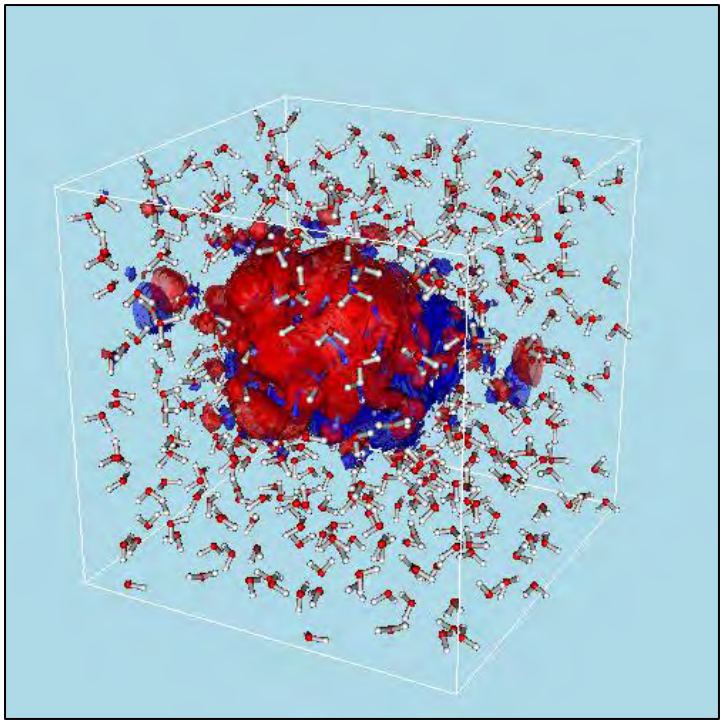
F.Gygi 2007

$(H_2O)_{512}$ states after bisection

localized

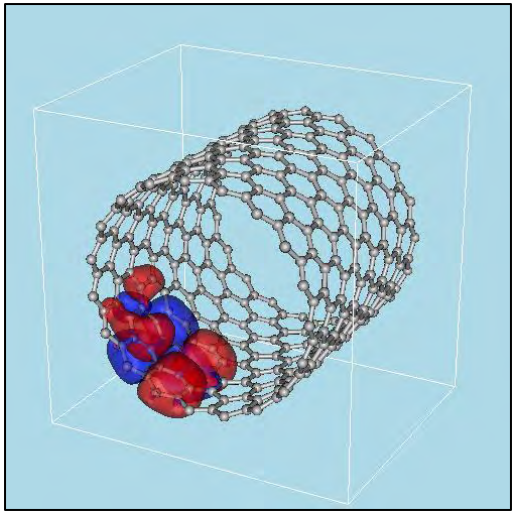


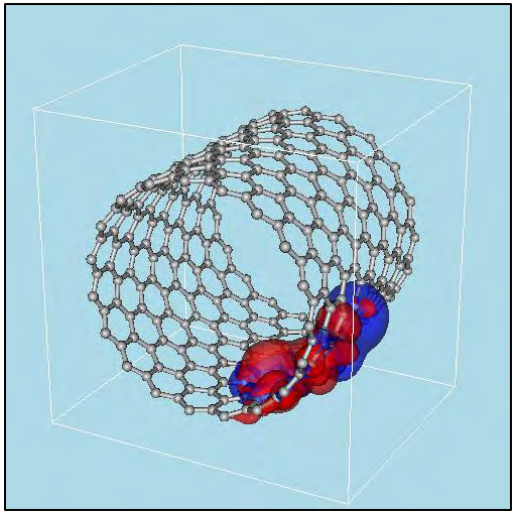
extended



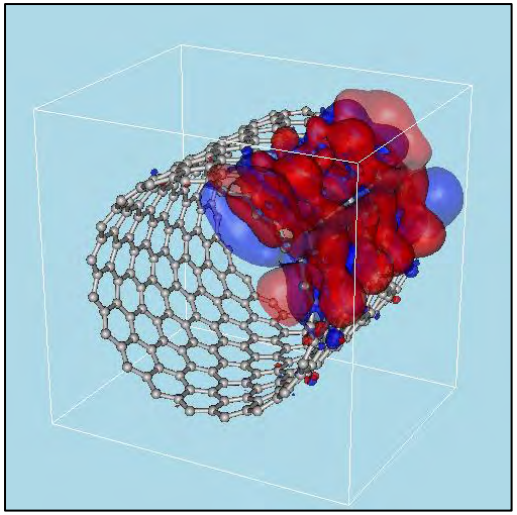
CNT(19x0) states after bisection

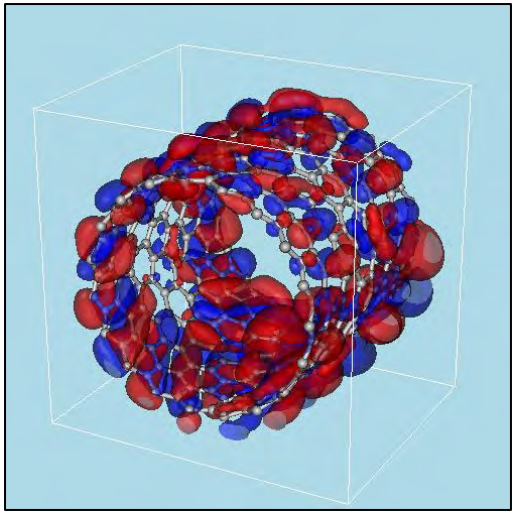
localized





extended





Predictive modeling with controllable accuracy

Ab-initio **Molecular Dynamics (DFT/GGA):**

Ground State Properties: Structural, electronic and vibrational, and in some cases thermodynamic and dynamical properties

Quantum Monte Carlo calculations: Optical Gaps and Total Energies

Many Body Perturbation Theory (GW): Spectra

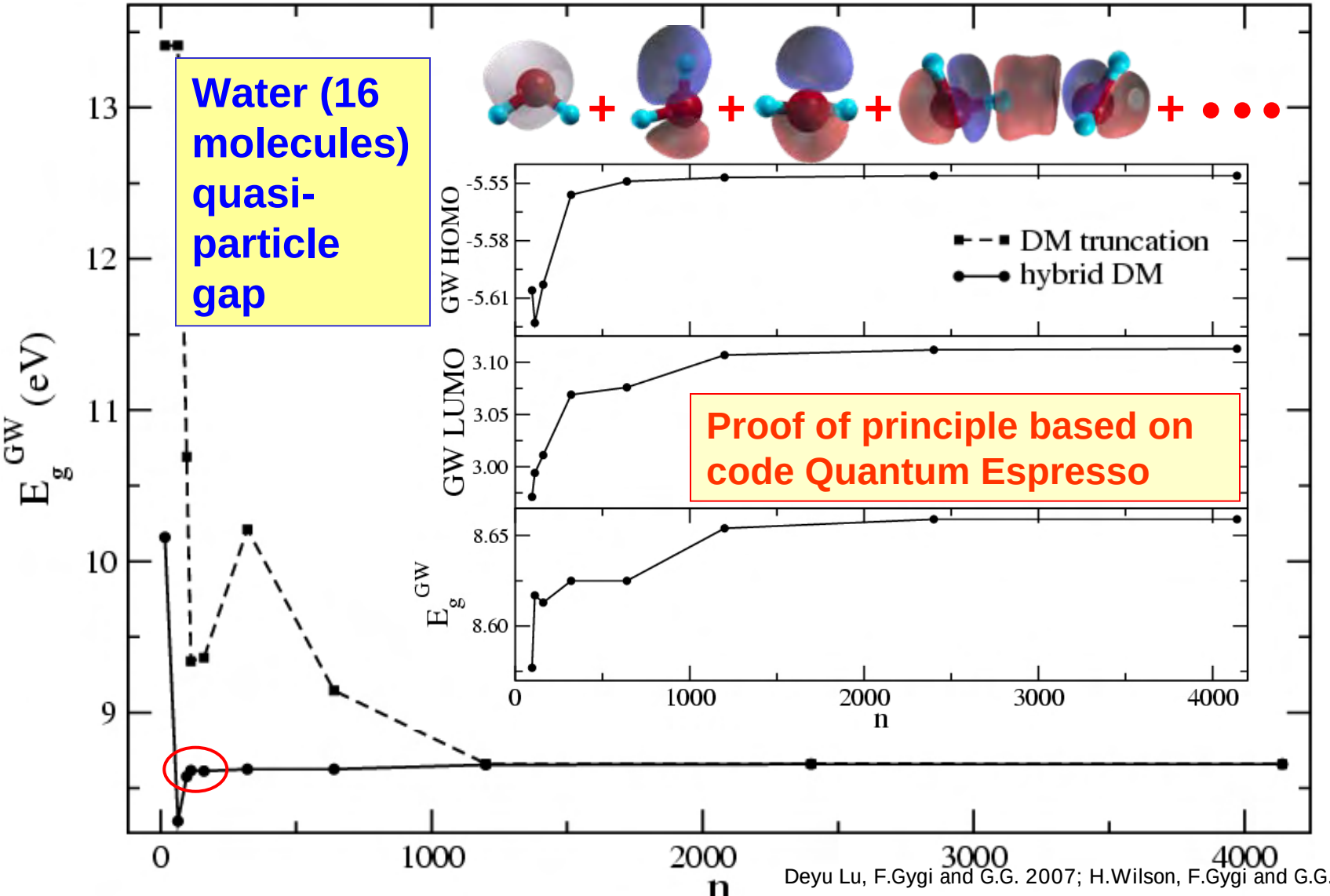
Excited State properties

Compute dielectric matrices

$$\Sigma = iG(1,2)W(1^+,2)$$

$$W(1,2) = \int d(3)\ \varepsilon^{-1}(1,3)v(3,2)$$

GW energy gap from approximate, yet accurate and non-empirical dielectric matrices



Deyu Lu, F.Gygi and G.G. 2007; H.Wilson, F.Gygi and G.G. 2007

Predictive modeling with controllable accuracy

Ab-initio Molecular Dynamics (DFT/GGA):

Ground State Properties: Structural, electronic and vibrational, and in some cases thermodynamic and dynamical properties

External electric and magnetic fields

Quantum Monte Carlo calculations: Optical Gaps and Total Energies

Many Body Perturbation Theory (GW): Spectra

Excited State properties

Classical and Path Integral Monte Carlo

Thermodynamic properties

Generalization of ab-initio MD in a magnetic field to generic supercells: W. Cai, G.Galli et al. J.Comp.Phys.2007

NMR spectra calculations– N.Marzari et al. 2007

Ab-initio theory of metal-insulator interfaces in finite electric field, N. Spaldin et al. Phys. Rev. B (2007).

Coupling of codes **Qbox** and **QMCPack** in progress—proof of principle for classical MC achieved: D.Ceperley, F.Gygi et al.

Water at the interface

•We are studying water in different environments: from small ion and Si quantum dot solvation to wetting of surfaces in extended and confined media.

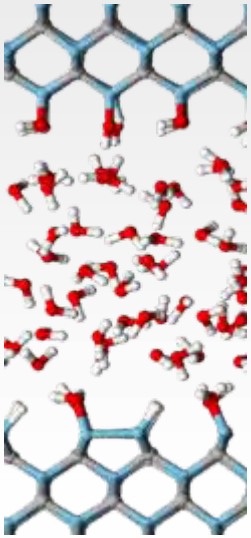
•We address fundamental issues regarding the atomic, electronic and dynamical properties of interfacial water.

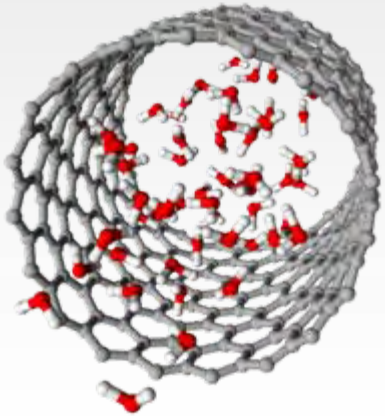
Hydrophilic surface SiC

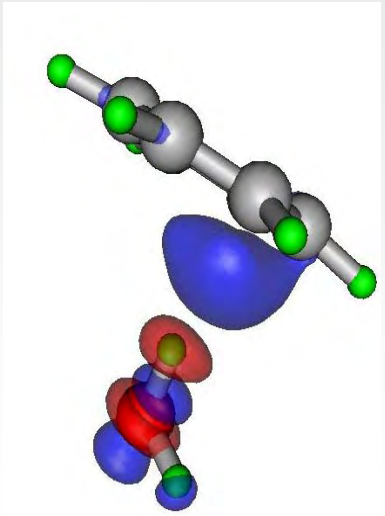
Hydrophobic surfaces – graphite, CNT and hydrogenated diamond

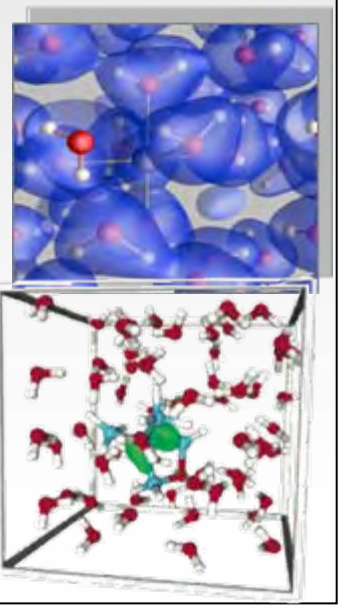
Hydrophobic solutes (benzene)

Solvation of ions and Si clusters



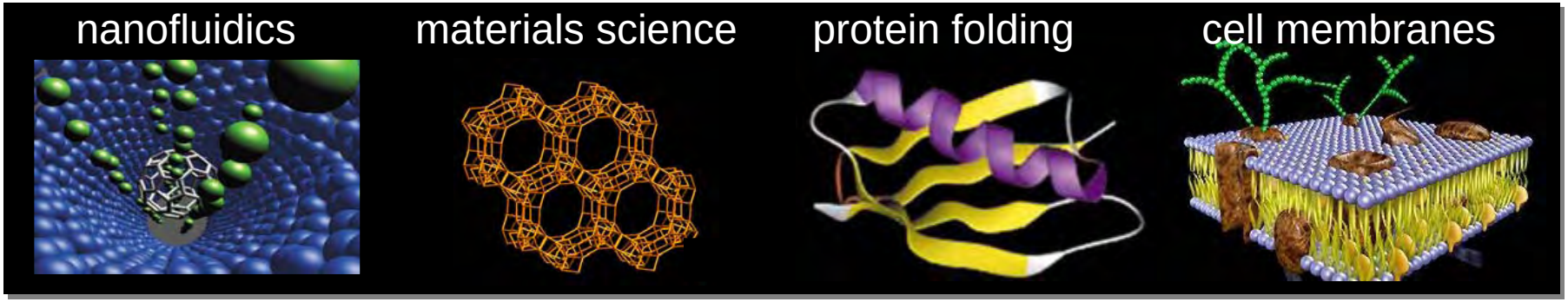






D.Prendergast et al., JACS 2004; G.Cicero, J.Grossman, A.Catellani and G.G., JACS 2005; M.Allesch, E.Schwegler and G.G., JPC-B 2007 and JCP (accepted); G.Cicero, J.Grossman, E.Scjwegler, F.Gygi and G.G. (submitted); M.Sharma, D.Donadio, E.Schwegler and G.G. (submitted).

Liquid water in confined media

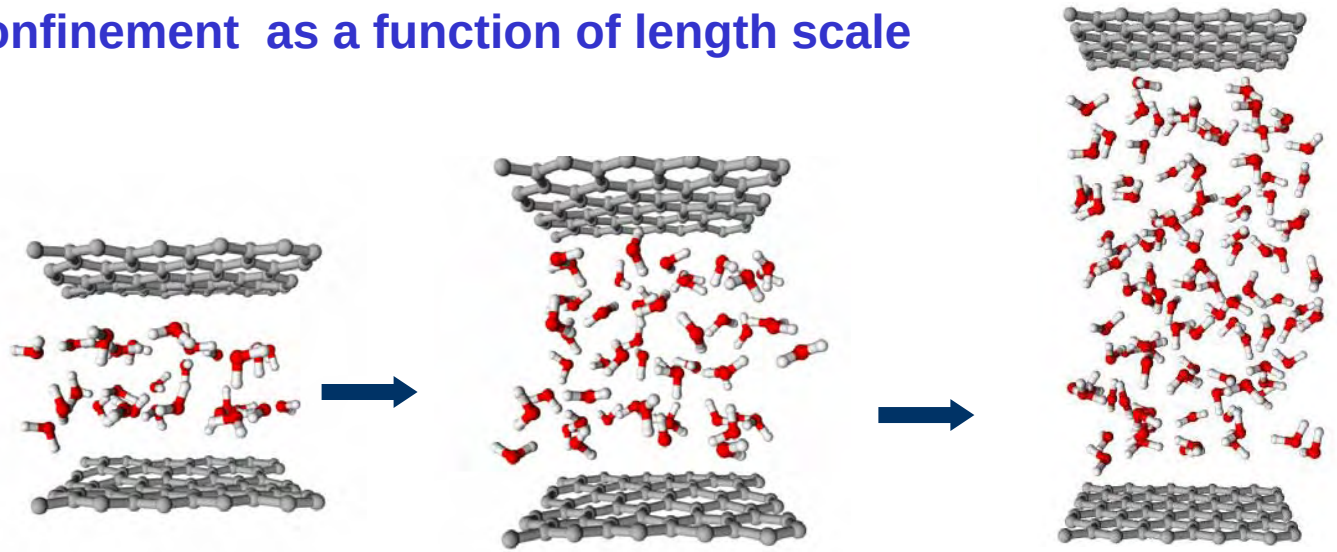


Understanding how the physical properties of bulk water (e.g. hydrogen bond network, diffusion, freezing point) are modified under confinement is relevant to a variety of outstanding scientific problems, including:

- » Studies of stability and enzymatic activity of proteins
- » Oil recovery
- » Nano-fluidics
- » Heterogeneous catalysis (role of water-substrate interaction)
- » Corrosion inhibition

Computational Strategy

Confinement as a function of length scale



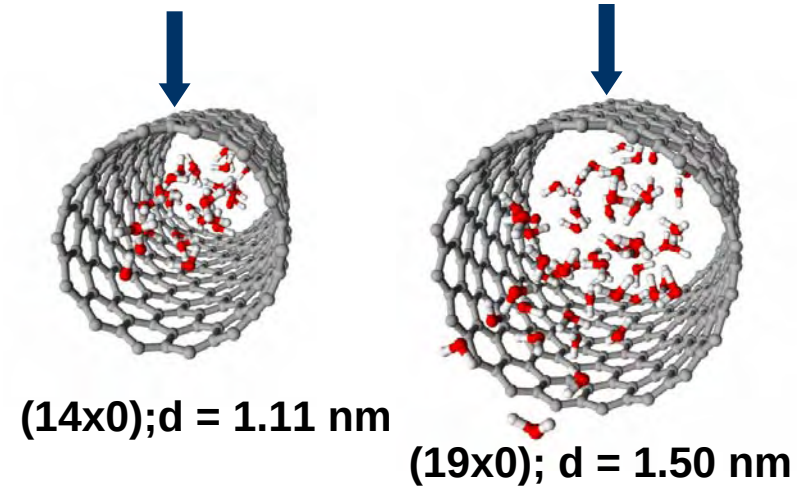
d = 1.01 nm

d = 1.44 nm

d = 2.50 nm

- Simulation time : 20-25 ps, except for graphene with d=2.50 nm (10 ps).
- We used D instead of H for computational convenience.

Confinement in more than one dimension



(14x0);d = 1.11 nm

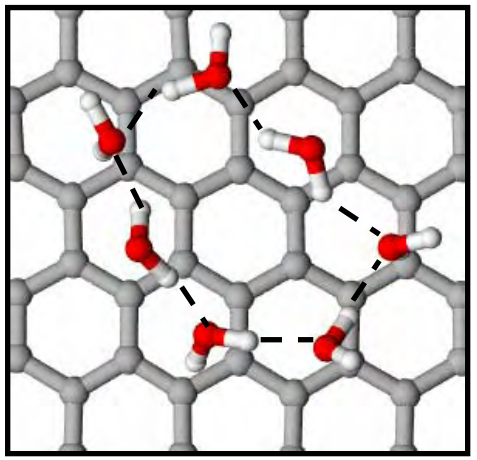
(19x0); d = 1.50 nm

Surface	# Water Molec.	# e-
None	64	512
SiC	57	1288
Graphite	32	496
Graphite	54 (49)	672
Graphite	108	1104
(14,0) CNT	34	1616
(19,0) CNT	54	1648

G.Cicero, J.Grossman, E.Schwegler, F.Gygi and G.G. submitted (2007)

Water confined within graphene and nanotubes

- **Perturbation induced by confinement is local**
- **No ice-like layer at the interface: liquid density increases**
- **Rarefaction and decrease of density away from the interface**
- **Dipole moment of water molecule at the interface decreases(*) → lateral diffusion is enhanced and re-orientational dynamics is faster: *Consistent with rapid flow in nanotubes detected in recent experiments***



Sticky yet fast water molecules at the interface

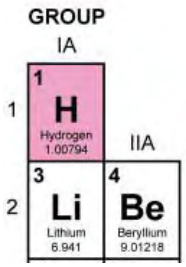
- **We predict that effects of OH bonds not engaged in hydrogen bonding and changes in librational modes are visible (although weak) in IR spectra.**

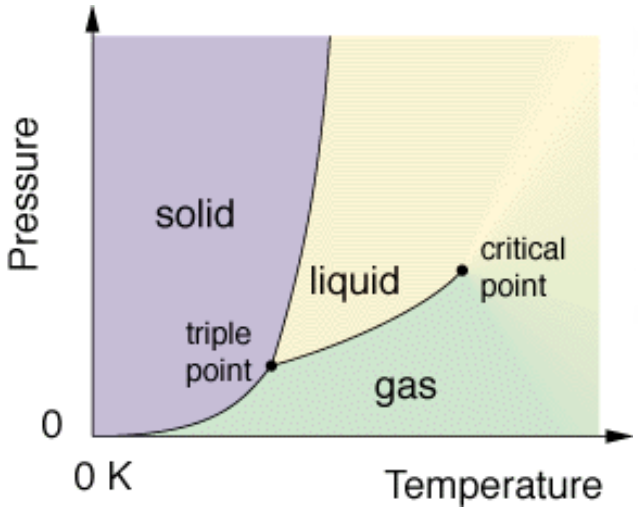
Complex electronic interactions occurs at the interface

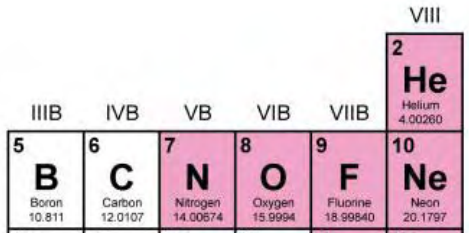
G.Cicero, J.Grossman, E.Schwegler, F.Gygi and G.G. 2007 (submitted); M.Sharma, E.Schwegler, D.Donadio and G.G. 2007 (submitted).

(*) Consistent with results obtained for Benzene and HFB in water: M.Allesch, E.Schwegler and G.G. JPC-B 2007.

Understanding phase diagrams of elements and ‘simple’ compounds



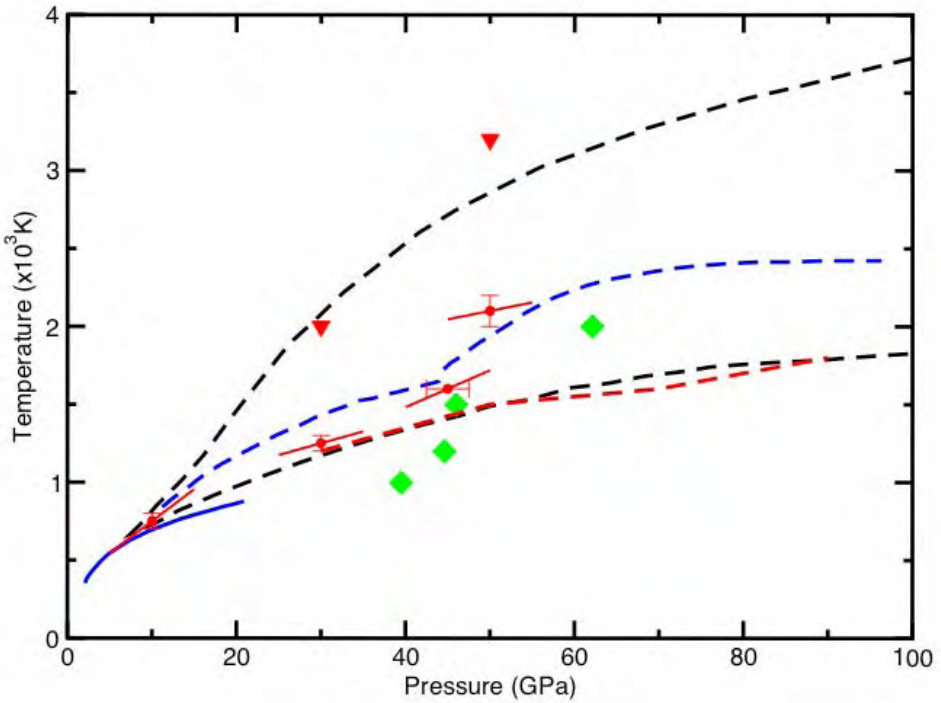




- **Difficult to tame: Does diamond melt?**
- **Hydrogen: a liquid ground state at zero T and high P?**
- **A spin glass of oxygen molecules ?**
- **Boron: is there a crystalline ground state?**

Melting of water under pressure

- Interpretation of experiments and understanding of melting processes
- Solution of existing controversies



E.Schwegler, F.Gygi and G.G. 2007

Work on more complex oxides and metal-oxides by W.Pickett et al. – beyond DFT, using Dynamical Mean Field Theory

Towards quantum engineering of materials

Simulations of integrated materials with specific functions for realistic devices

↓

Understand, predict and design

↑

Complexity of *design* lies both in defining strategies and algorithms to compute novel properties and in optimizing simultaneously several, interrelated physical and chemical variables.

Additional complexity in software design and optimization.

Some of the most pressing scientific challenges of our age…

Researchers funded through the Office of Science are working on some of the most pressing scientific challenges of our age including: 1) Harnessing the power of microbial communities and plants for energy production from renewable sources, carbon sequestration, and environmental remediation; 2) Expanding the frontiers of nanotechnology to develop materials with unprecedented properties for widespread potential scientific, energy, and industrial applications; 3) Pursuing the breakthroughs in materials science, nanotechnology, biotechnology, and other fields needed to make solar energy more cost-effective; 4) Demonstrating the scientific and technological feasibility of creating and controlling a sustained burning plasma to generate energy, as the next step toward making fusion power a commercial reality; 5) Using advanced computation, simulation, and modeling to understand and predict the behavior of complex systems beyond the reach of some of our most powerful experimental probes, with potentially transformational impacts on a broad range of scientific and technological undertakings; 6) Understanding the origin of the universe and nature of dark matter and dark energy; and 7) Resolving key uncertainties and expanding the scientific foundation needed to understand, predict, and assess the potential effects of atmospheric carbon dioxide on climate and the environment.

R.Orbach, Subcommittee on Energy and Water Development, Senate Appropriations Committee, 3/21/07

Many thanks to my collaborators

Z.Bai, F.Gygi and W.Pickett, UCD

W. Cai, Stanford U.

D.Ceperley, UIUC

N.Marzari, MIT

N.Spaldin, UCSB

E.Schwegler and J.-L.Fattebert, LLNL.

Thanks for your attention and for the kind invitation

Computer time: ***INCITE AWARD (ANL and IBM@Watson),*** ***LLNL, NERSC, SDSC***