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Density Functional Theory (DFT) research at Sandia National Laboratories: from exchange-correlation functionals to a broad range of applications

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Naval Research Laboratory, Dec 9, 2010.

SAND: 2010-XXXXP

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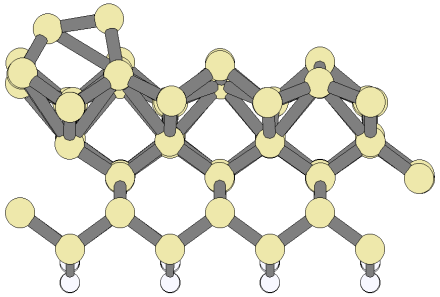
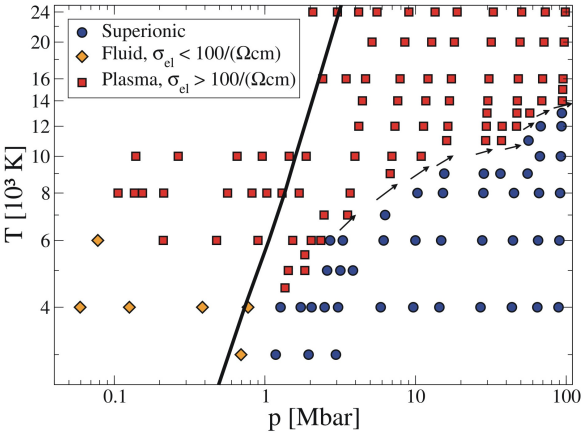
Common to these and many other systems is the importance of the electronic structure

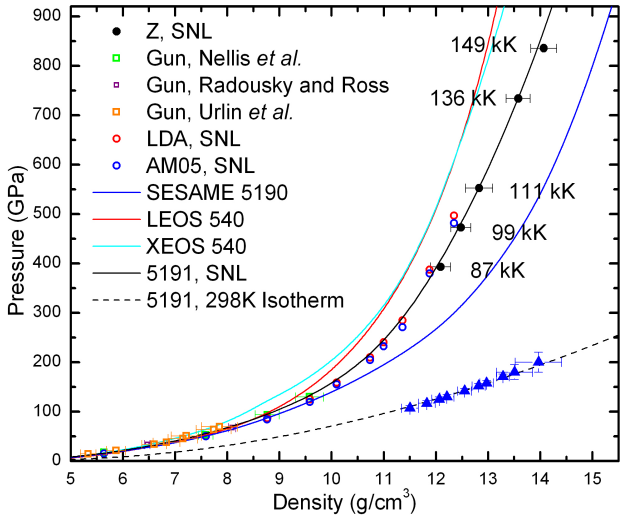


Surface dynamics on Si(001)

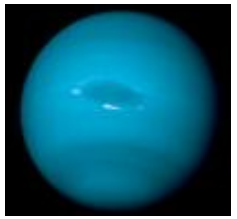
$$\psi_\nu(\boldsymbol{r})$$



Water under high energy-density conditions



Shock compression of liquid xenon



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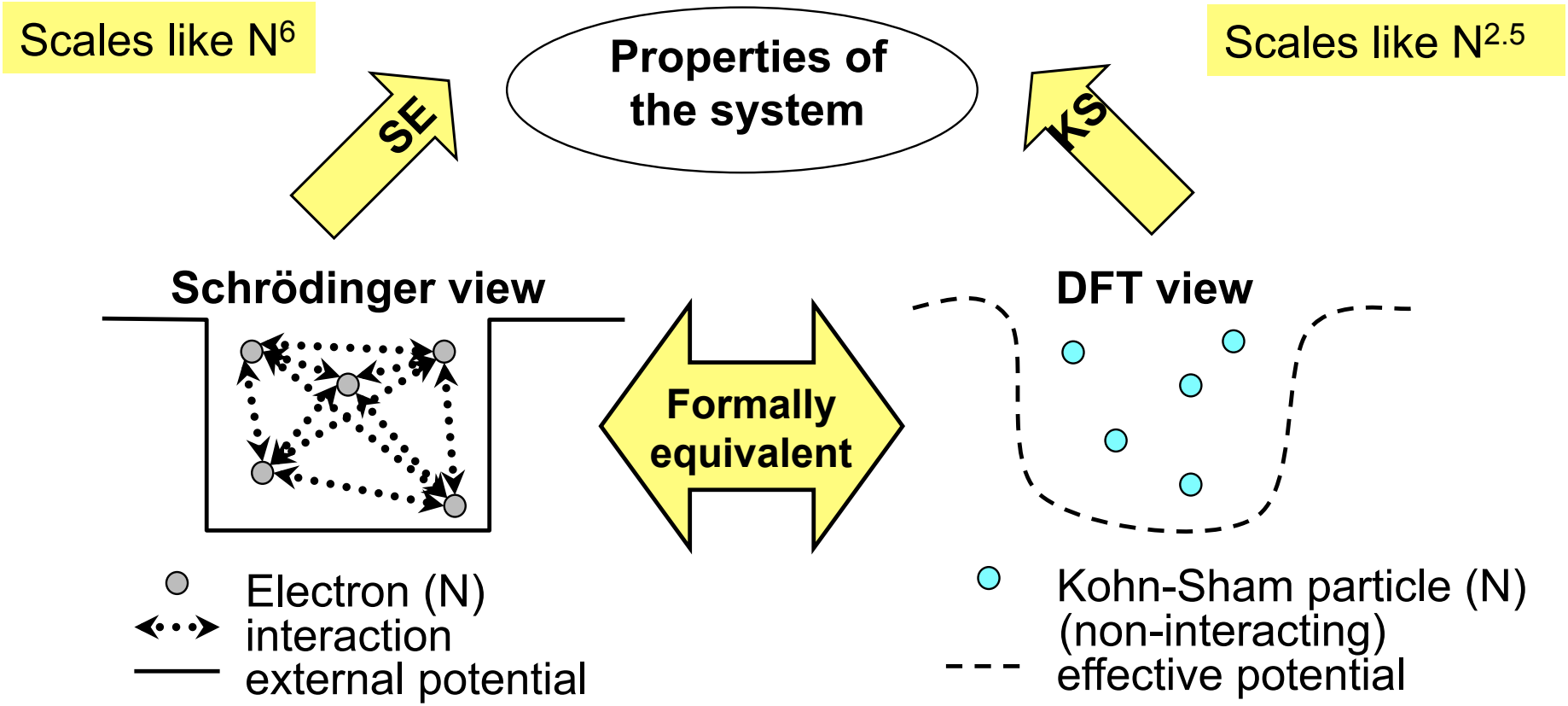
Dirac was optimistic as well as realistic in 1929

Dirac (1929)

“ The general theory of quantum mechanics is now almost complete … . The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. ”

P.A.M. Dirac, Proc. R. Soc. London Ser. A 123, 714 (1929).

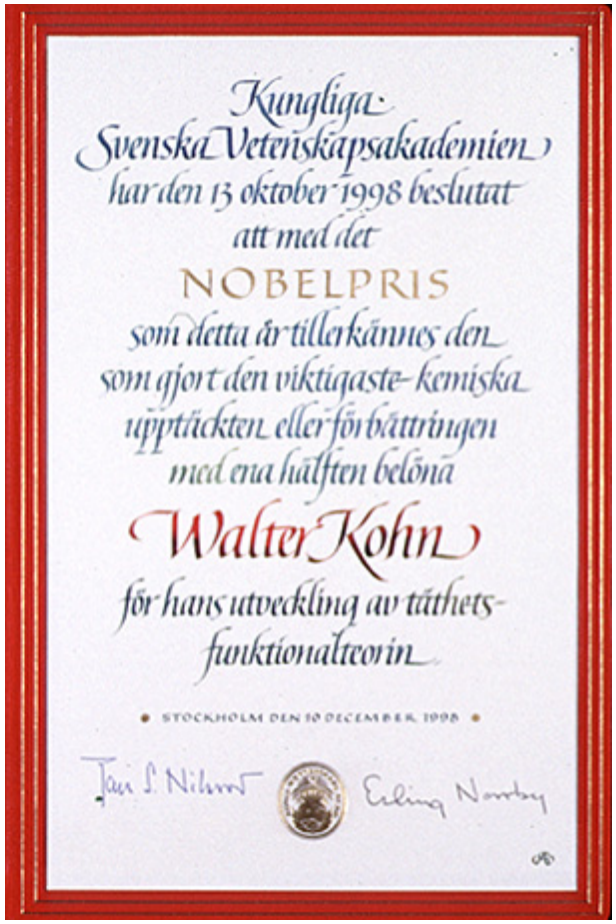
Density Functional Theory was a tremendous discovery, reducing the complexity of quantum calculations



Walter Kohn was awarded the 1998 Nobel Prize in Chemistry

Hohenberg-Kohn theorem:
Phys. Rev. **136**, B864 (1964).

Kohn-Sham equations:
Phys. Rev. **140**, 1133 (1965).



The Kohn-Sham equations reduce the many-body problem from (3N) dimensions to the three spatial (x,y,z)

$$\left(-\frac{\hbar^2}{2\,m}\nabla^2 + \mathrm{v}_{eff}(\boldsymbol{r})\right)\psi_\nu(\boldsymbol{r}) = \epsilon_\nu\,\psi_\nu(\boldsymbol{r}) \quad \nu = 1,\ 2,\ \ldots.,\ N$$

$$n(\boldsymbol{r}) = \sum_{\nu=1}^{N} |\,\psi_\nu(\boldsymbol{r})\,|^2$$

$$\mathrm{v}_{eff}(\boldsymbol{r}) = \mathrm{v}(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\,\boldsymbol{r}-\boldsymbol{r}'\,|}\,d\boldsymbol{r}' + \frac{\delta E_{xc}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}$$

The exchange-correlation (XC) functional determines the accuracy of each and every DFT calculation

$$E_{xc} = \int_V n(\boldsymbol{r})\, \epsilon_{xc}(\boldsymbol{r};[n])\, dV$$

The *exchange-correlation energy density* is modeled in DFT.

For a very long time, scientists working on applications in solid state physics in reality had one choice to make: LDA or PBE?

This shaped a lot of the thinking

Functional/year	Class	Use
LDA/1965 Wigner correl.	density	Model systems
LDA/1980 QMC correl. (CA)	density	Solid state
BLYP/1988	gradient	Molecules
PW91/1991	gradient	General w. molecule bias
B3LYP/1993	gradient + HF	Molecules
PBE/1996	gradient	General w. molecule bias
revPBE/1998	gradient	Refit PBE for atoms
RPBE/1999	gradient	Refit PBE for surface science

The XC functional sets the fundamental accuracy, but there are *additional numerical approximations* made

Wave-functions are expanded in a basis, plane-waves or local atomic.

Verify convergence with respect to plane-wave cutoff.

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(\boldsymbol{r})\right)\psi_\nu(\boldsymbol{r}) = \epsilon_\nu \psi_\nu(\boldsymbol{r}) \quad \nu = 1, 2, \ldots, N$$

$$n(\boldsymbol{r}) = \sum_{\nu=1}^{N} |\psi_\nu(\boldsymbol{r})|^2$$

$$v_{eff}(\boldsymbol{r}) = v(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' + \frac{\delta E_{xc}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}$$

Periodic systems are solved in k-space (Bloch's theorem / Brillouin zone).

Verify convergence with respect to k-point sampling.

The XC-functional and the numerical approximations are not in the same trade-space.

Shortcomings in XC can never be compensated by numerical settings.

Core electrons are not important for bonding, treat only the valence electrons.

The pseudo-potential used should give a faithful description of the all-electron potential.

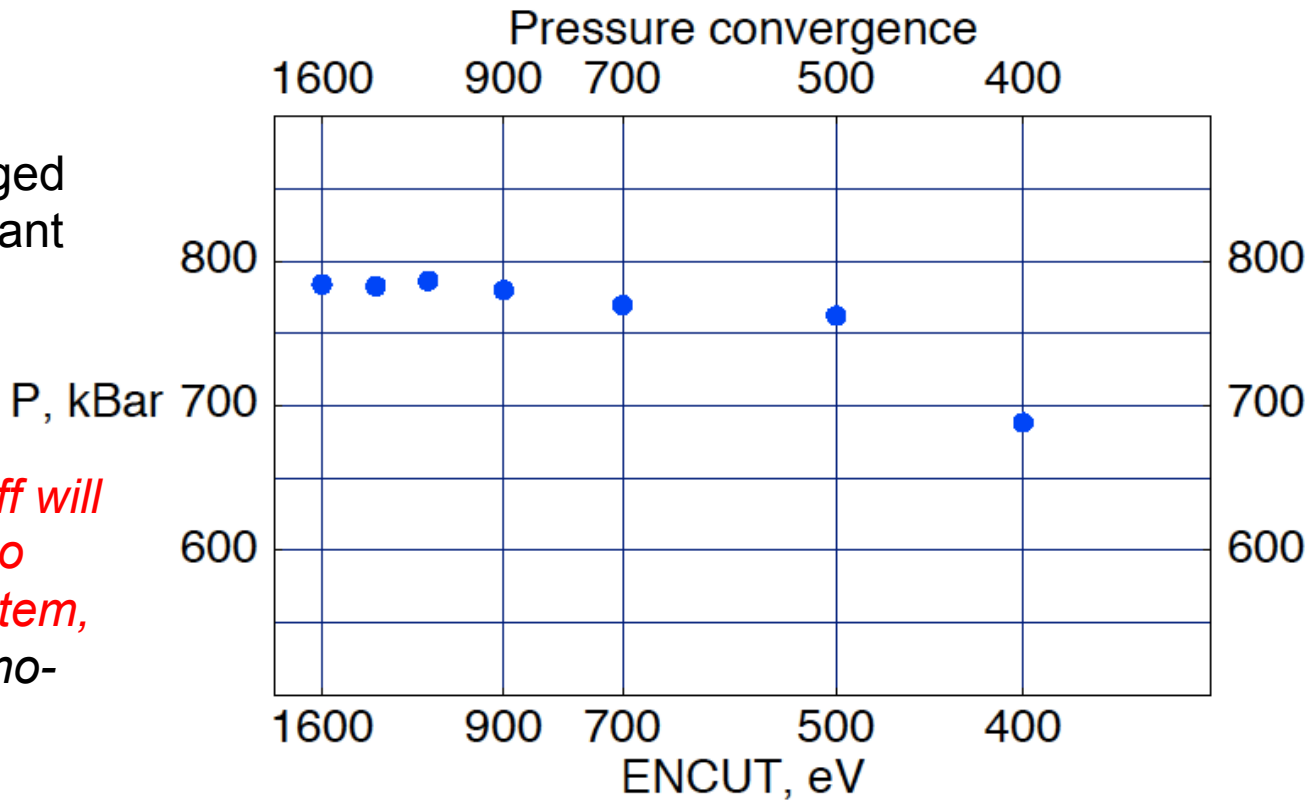
A. E. Mattsson et al. *"Designing meaningful density functional theory simulations in materials science – a primer"* Modelling and Simulation in Materials Science and Engineering **13**, R1 - R31 (2005).

Convergence with respect to plane-wave cutoff energy is essential for first-principles thermodynamics calculations

Water at 4000 K and 2.5 g/cm^3

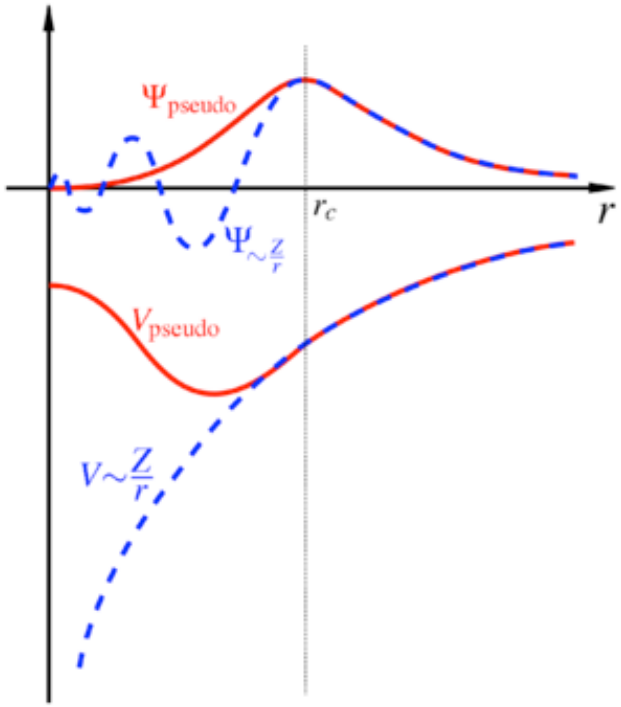
The plane-wave energy cutoff should be converged with respect to the relevant property.

Calculations at low cutoff will give a systematically too low pressure for the system, very important for thermo-dynamics



Phase Diagram and Electrical Conductivity of High Energy-Density Water from Density Functional Theory, T. R. Mattsson and M. P. Desjarlais, Phys. Rev. Lett. **97**, 017801 (2006).

Pseudo-potentials give an approximation to the full-core potential and are not for tuning



The pseudo- and true wave functions are identical for distances larger than r_C

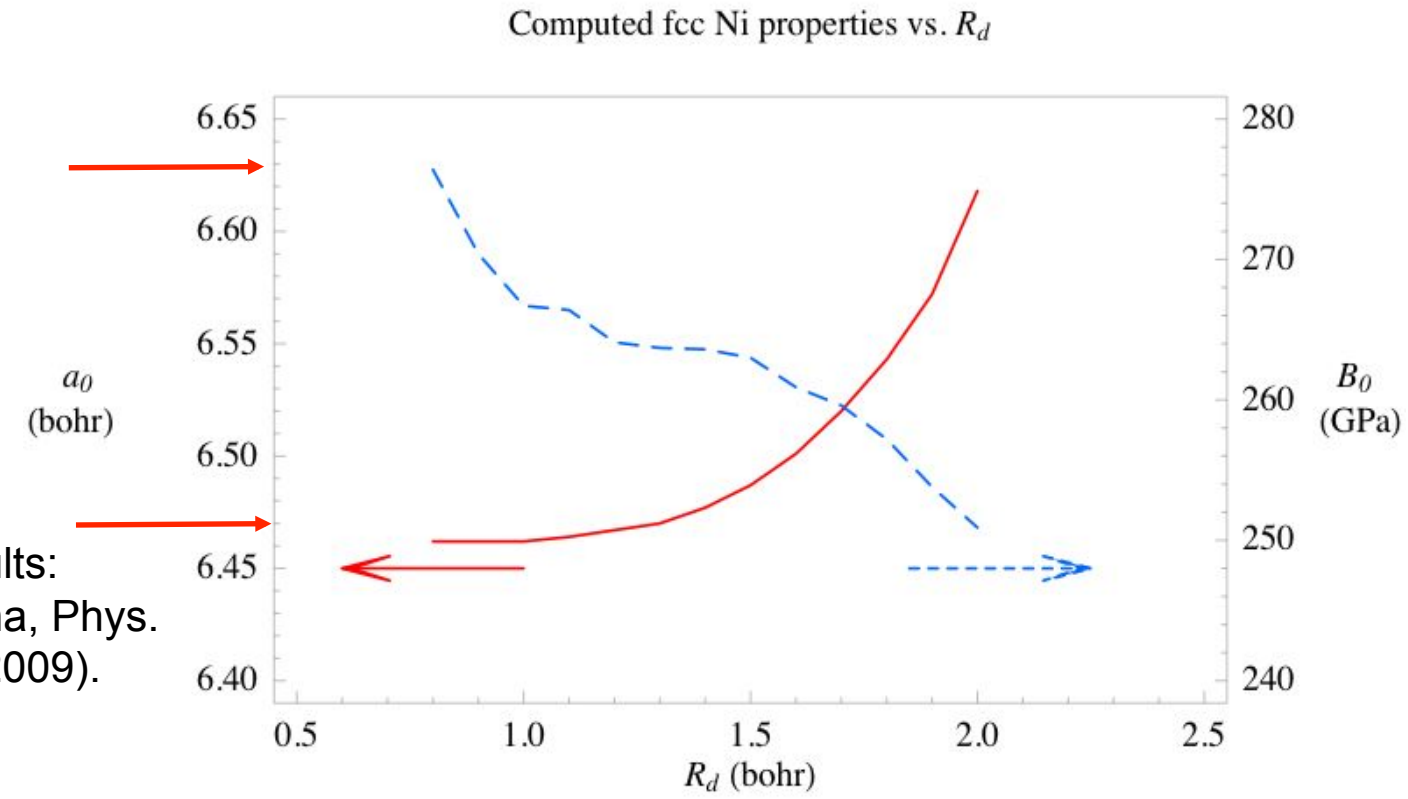
Smaller r_C yield a solution that is more like the real one, but results in a more demanding calculation

r_C is the 'core radius parameter', one of the main parameters to set when constructing a pseudopotential.

Pseudo-potentials give an approximation to the full-core potential and are not for tuning

Experimental value

All-electron LDA results:
Haas, Tran, and Blaha, Phys. Rev. B **79**, 085104 (2009).



How good a pseudo potential is should be determined by how well it reproduces the results from all-electron calculations.

R_d is the 'core radius parameter'

A. E. Mattsson et al. Modelling and Sim. in Mat. Sci. and Eng. **13**, R1-R31 (2005).

We are no longer limited by the traditional choice between LDA and PBE when doing solid state physics

Lattice constants (A)

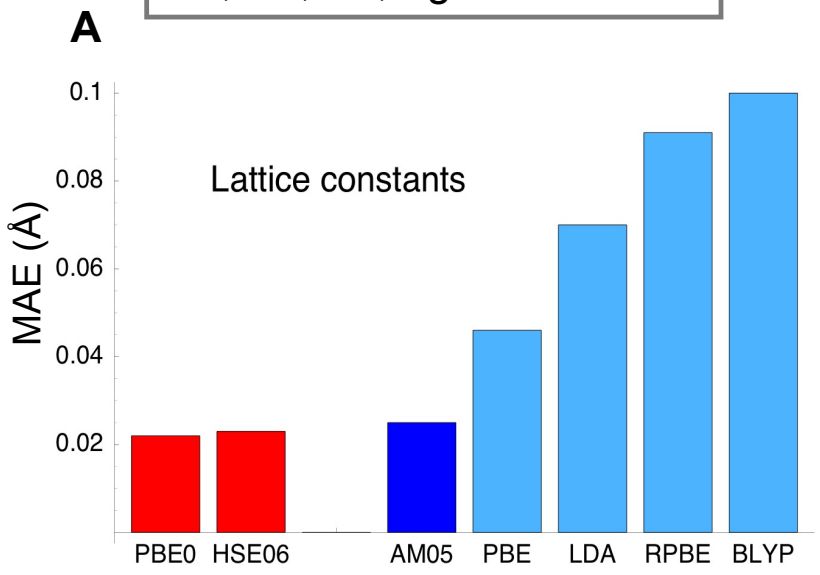
Solid	LDA	PBE	BLYP	Exp	AM05
C	3.534	3.573	3.598	**3.567**	3.551
SiC	4.330	4.377	4.411	**4.358**	4.350
Ag	4.001	4.150	4.262	**4.069**	4.054
MgO	4.168	4.259	4.281	**4.207**	4.232
Bias	Short	Long	Longer		No bias
Mean E	-0.07	+0.039	+0.093		+0.001
Mean |E|	0.07	0.046	0.100		0.025

"Functional designed to include surface effects in self-consistent density functional theory",
A.E. Mattsson and R. Armiento, Phys. Rev. B **72**, 085108 (2005).

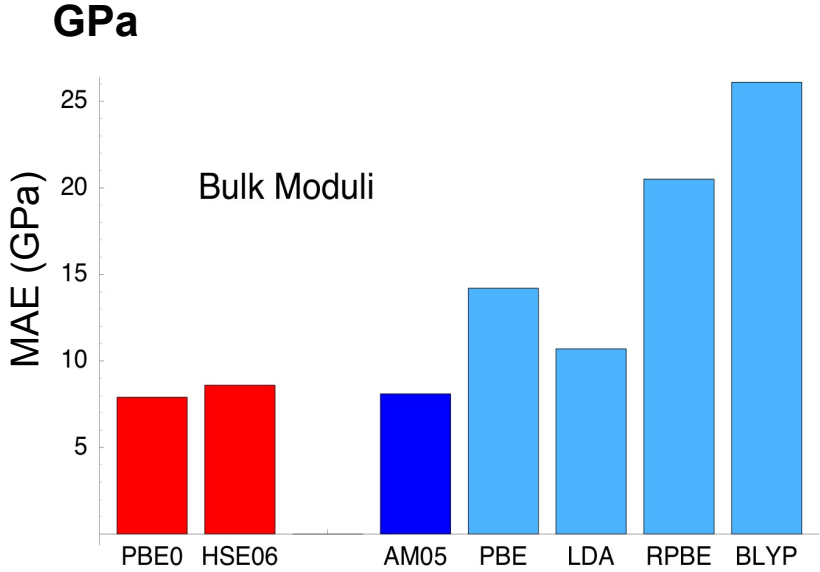
A new level of accuracy using the new XC functional AM05: benchmark for 20 solids

Li, Na, Al,
BN, BP, C, Si, SiC,
β-GaN, GaP, GaAs,
LiF, LiCl, NaF, NaCl, MgO,
Cu, Rh, Pd, Ag.

AM05 performs as well for solids as the hybrids HSE and PBE0 do, while being 60-1000 times less expensive in computer time.
Accurate and fast is possible



Mean absolute error: lattice const.



Mean absolute error: bulk moduli.

The AM05 density functional applied to solids, A. E. Mattsson, R. Armiento, J. Paier, G. Kresse, J. M. Wills, and T. R. Mattsson, J. Chem. Phys. **128**, 084714 (2008).

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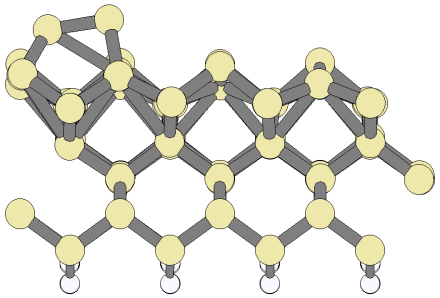
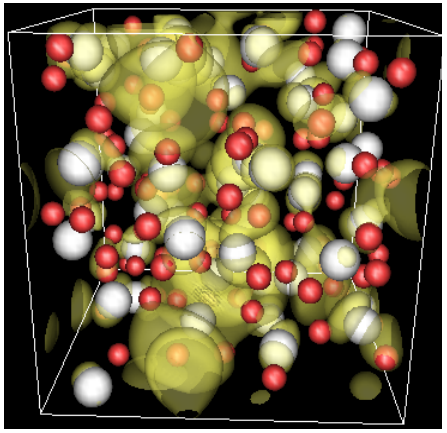
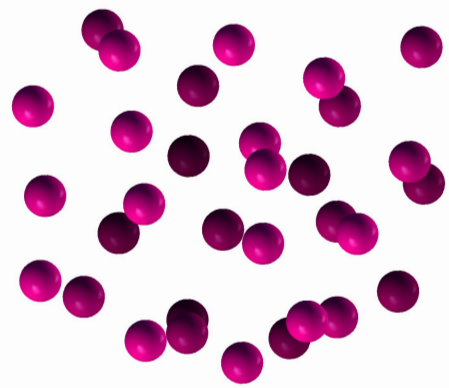
Common to these and many other systems is that calculations on a hundred or so atoms can give answers



96 Si atoms and 16 H can be used to study surface diffusion on Si.



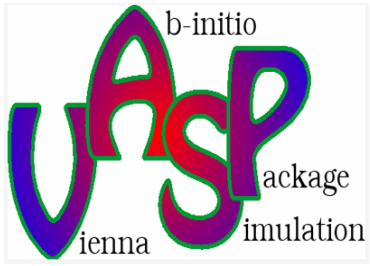
32 – 64 water molecules describe a lot of the thermodynamics of water under conditions found in the giant planets.



Quantitative results for shock compression of liquid xenon are obtained with 32 Xe atoms

What can you learn about your system if you know the structures, energies, and processes for 100 - 200 atoms?

Density functional theory (DFT) based MD is our work-horse for calculating materials properties



- VASP 5.2 code (Georg Kresse, Vienna, Austria)
- Plane-wave basis-set
- *Finite-temperature DFT (Mermin) is crucial for thermodyn.*
- Projector augmented wave core functions (PAW)

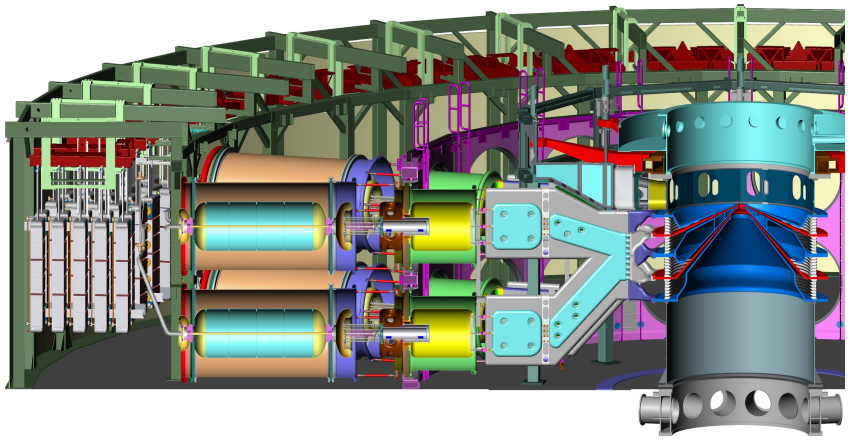
- **Long MD simulations, tens of thousands of steps**
- *Yield equilibrium thermodynamics: $P(\rho,T)$, $E(\rho,T)$, g(r), structure, and diffusion*

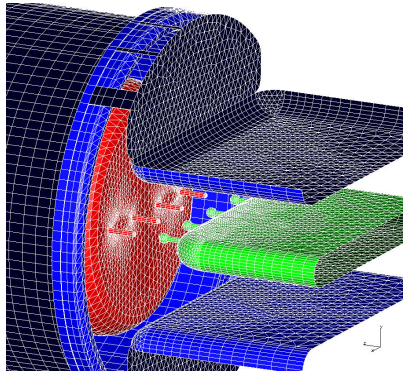
- **Snapshots from MD runs**
- *Transport properties like electrical- and thermal conductivities via linear response*

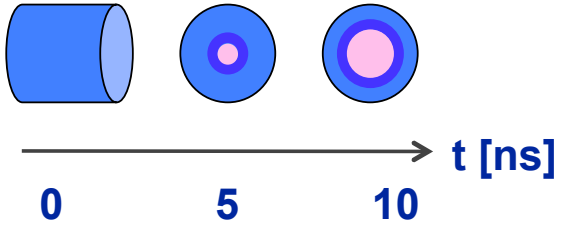
- Mainly Sandia High Performance Computing (HPC): red sky, red storm, glory, unity

- Research in fundamental DFT: **http://dft.sandia.gov**
  - Ann Mattsson, Anatole von Lilienfeld, Rudy Magyar
  - Subsystem functional approach (AM05)

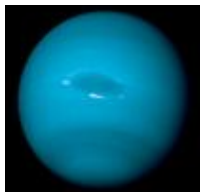
Properties of shocked water is of direct interest to Sandia as well as of general scientific interest.







- Water switches as pulse-shaping components
- Water tampers at exploding wire experiments
- Shock-waves in water
- Planetary interiors



Water at 300 K and 1 g/cm^3; 10 ns later:

× 50 density (0.05 to 2.5 g/cm^3).

×100 temperature (2500 to 300 000 K).

Demanding range of conditions.

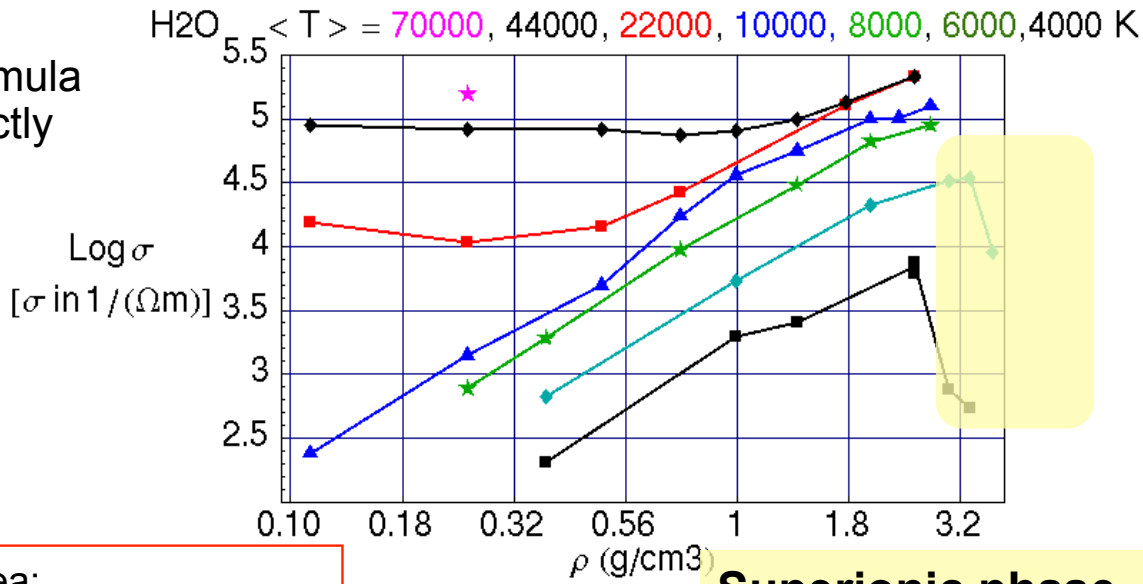
Conductivity in water -- electronic conduction from the Kubo-Greenwood formula.

$$\sigma_{\mathbf{k}}(\omega) = \frac{2\pi e^2 \hbar^2}{3m^2 \omega \Omega} \sum_{\alpha=1}^{3} \sum_{j=1}^{N} \sum_{i=1}^{N} (F(\varepsilon_{i,\mathbf{k}}) - F(\varepsilon_{j,\mathbf{k}})) \left| \left\langle \Psi_{j,\mathbf{k}} \left| \nabla_\alpha \right| \Psi_{i,\mathbf{k}} \right\rangle \right|^2 \delta(\varepsilon_{j,\mathbf{k}} - \varepsilon_{i,\mathbf{k}} - \hbar\omega),$$

Sum over bands **Fermi weights** **Dipole matrix element** **Energy conservation**

- Wave-function based[1]
  - Kubo-Greenwood (KG) formula yields the conductivity directly from wave-functions
  - Neither cross-sections nor relaxation times required
- Range in this work:
  - 0.1 - 3.3 g/cm^3
  - 4000 - 70 000 K.

DC electronic conductivity of water



Superionic phase

First application of K-G DFT to HEDP area:
[1]Desjarlais, Kress, and Collins, PRE **66**, R025401 (2002).

Wide-range modeling of conductivity in water:
Mattsson and Desjarlais, PRL **97**, 017801 (2006).

Conductivity in water -- proton conduction from QMD simulations of proton diffusion.

Classical Kubo expression for proton conductivity:

$$\sigma = \frac{ne^2}{m}\int_0^\infty \frac{\langle v(\tau)v(0)\rangle}{\langle v(0)v(0)\rangle}d\tau$$

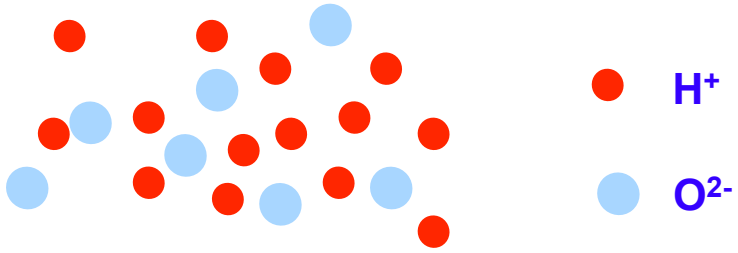
- Valid when all protons are free/equivalent.

Reduction due to H_2O diffusion

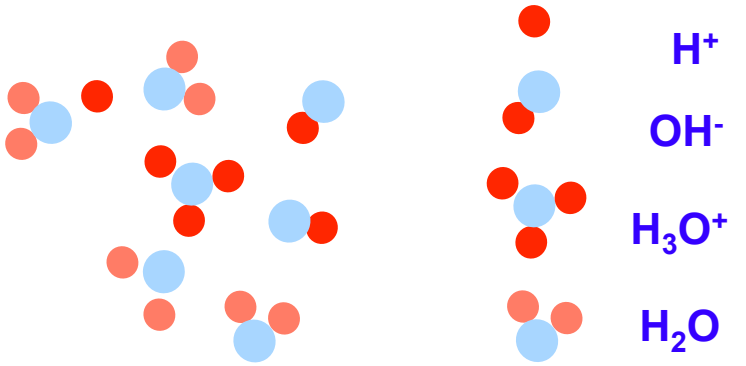
$$D_H = (1-\gamma)D_{H^*} + \gamma D_O$$

$$D_{H^*} = \frac{1}{1-\gamma}\left(1-\gamma\frac{D_O}{D_H}\right)D_H$$

γ -- fraction H atoms bound as H_2O.
D_H -- diffusion ALL H atoms.
D_{H^*} -- diffusion all H species but H_2O.



Full dissociation, all protons contribute.



Diffusion as H_2O is non-conducting.

Wide-range modeling of conductivity in water:
*Mattsson and Desjarlais, PRL **97**, 017801 (2006).*

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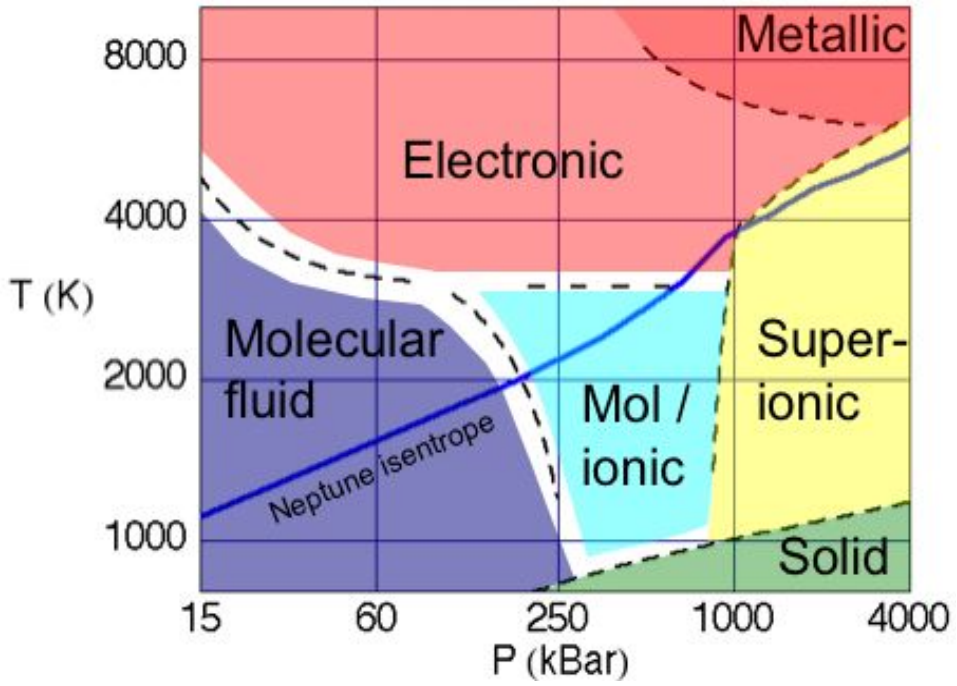
PRL 2006: Phase-diagram of HEDP water: notable revisions from previous theory

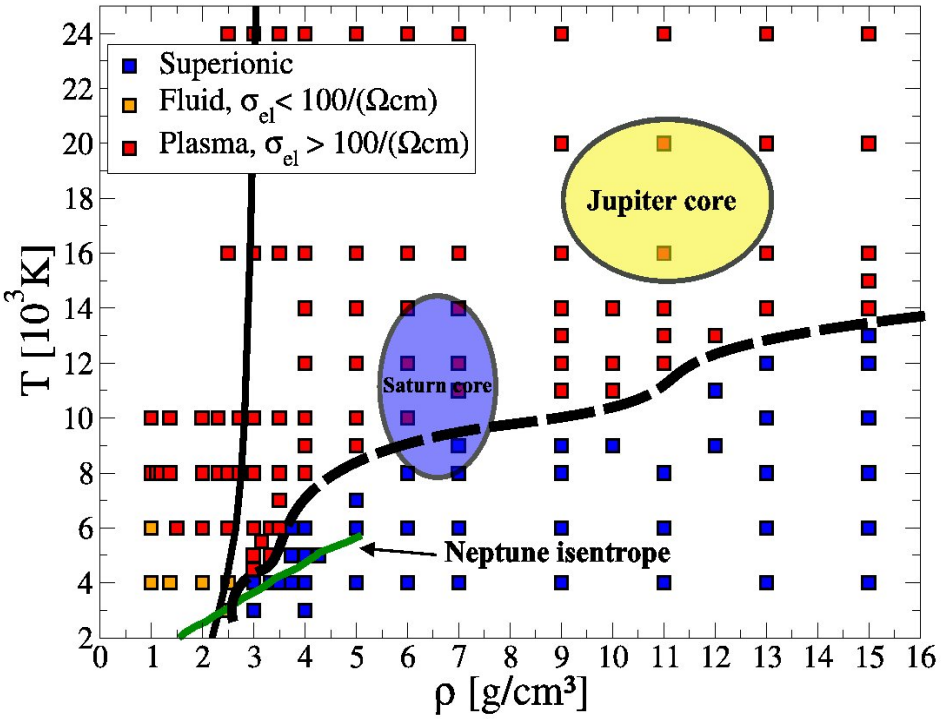


- Direct transition from superionic to conducting fluid at 100 GPa, 4000 K
- Electronic conduction over a large region previously described as insulating (Cavazzoni et al. Science 283, 44 (1999)
- Superionic phase boundary at higher pressure, 100 GPa at 2000 K, thus confirming findings by N. Goldman et. al. PRL **94**, 217801 (2005)

Revision of a large region of the phase-diagram, including a significant range of the Neptune isentrope.

Full consequences yet to be determined (SCCM *2007*)

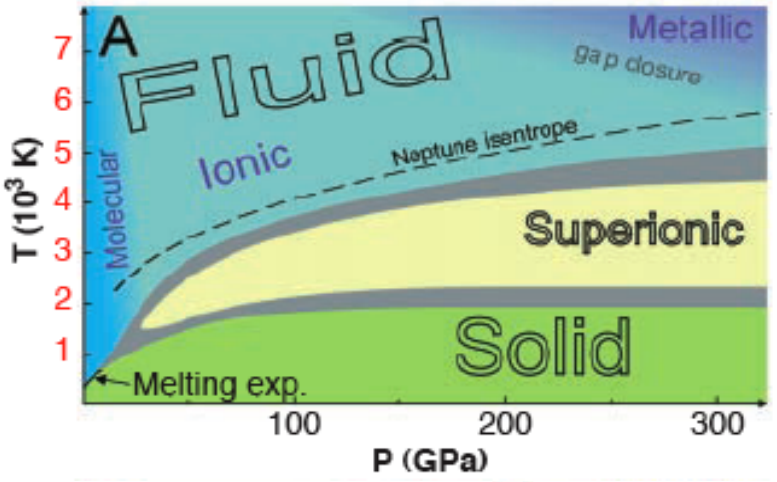
PRB 2009: Phase-diagram of HEDP water: extended the range and quantitative grid



Equation of state and phase diagram of water at ultrahigh pressures as in planetary interiors
M. French, T. R. Mattsson, N. Nettelman, and R. Redmer, Phys. Rev. B **79**, 054107 (2009).

- Core of Jupiter in the dense plasma regime
- Saturn core differ between models but majority of core is dense plasma
- Superionic/plasma phase boundary shows a kink at high density
- *Water in Neptune's core is most likely superionic*

Cavazzoni, et. al. (Science 283, 44 (1999))



Basic equations for planetary modeling

Mass conservation:

$$dm = 4\pi r^2 \rho(r)\, dr$$

Hydrostatic equation of motion:

$$\frac{1}{\rho}\frac{dP}{dr} = \frac{dU}{dr}\ , \qquad U = V + Q$$

Gravitational potential:

$$V(\vec{r}) = -G\int_{V_0} d^3r' \frac{\rho(r')}{|\vec{r} - \vec{r}'|}$$

Expansion into Legendre polynomials:

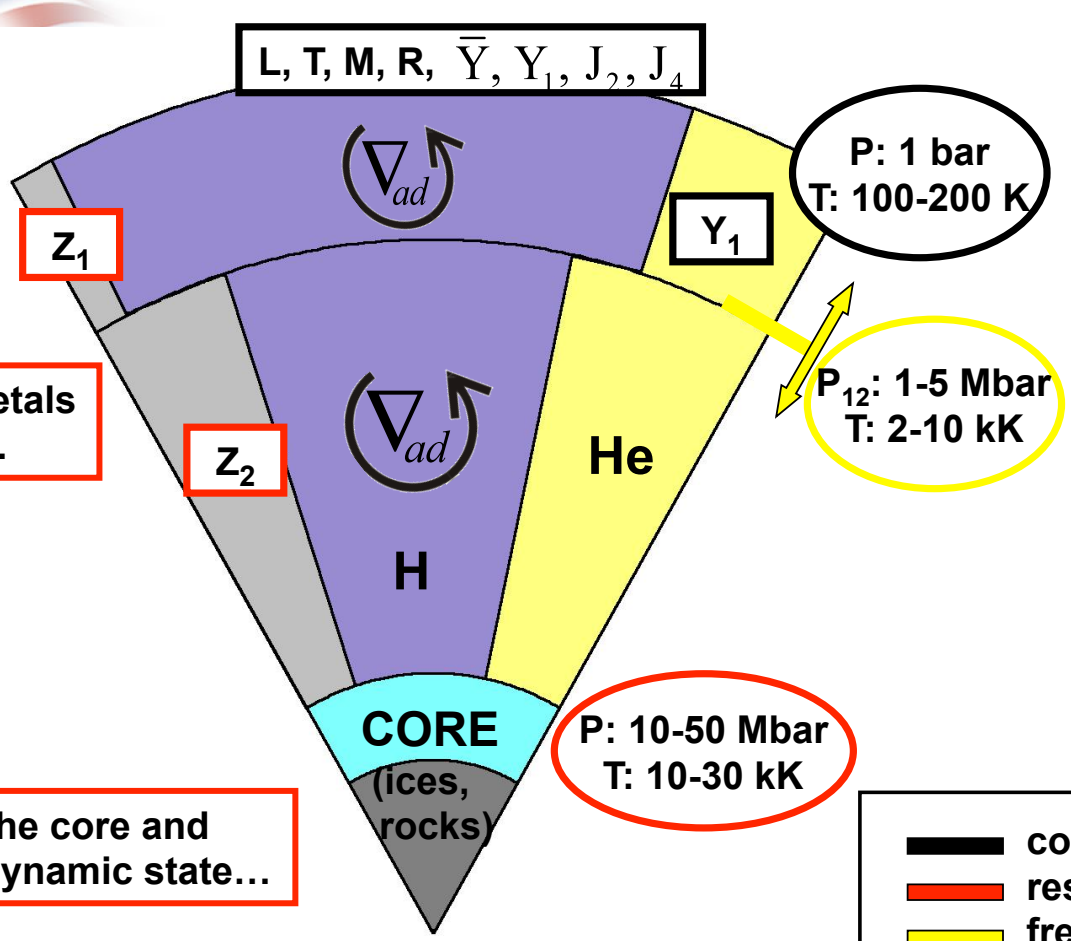
$$V(r,\theta) = -\frac{GM}{r(\theta)}\left(1 - \sum_{i=1}^{\infty}\left(\frac{R_{eq}}{r(\theta)}\right)^{2i} J_{2i} P_{2i}(\cos\theta)\right)$$

Gravitational moments:

$$J_{2i} = -\frac{1}{MR_{eq}^{2i}}\int d^3r'\, \rho(r'(\theta'))\, r'^{2i}\, P_{2i}(\cos\theta')$$

Accurate EOS data for warm dense H, He and the representative of metals (H_2O) is the most important input!

Standard three-layer structure model for GPs



P: 1 bar
T: 100-200 K

P_{12}: 1-5 Mbar
T: 2-10 kK

P: 10-50 Mbar
T: 10-30 kK

Y: fraction of He

Z: fraction of metals

J_2, J_4: gravitational moments

Fraction of metals in the layers…

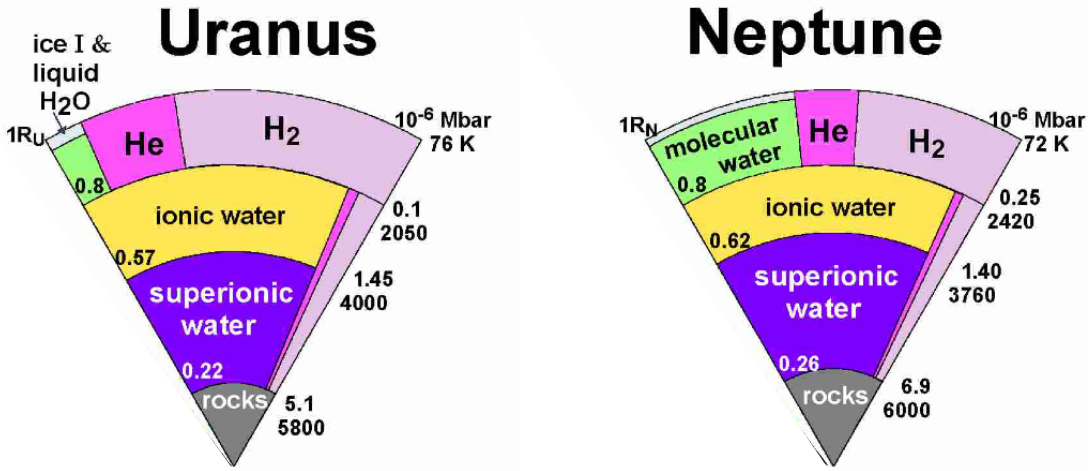
Physical origin and location of the layer boundary…
→ MIT (PPT)
→ H-He demixing

Size of the core and thermodynamic state…

constraints
results from modeling
free parameter

Interior structure models of this type are uniquely defined by the observables, except P_{12}

Interior of Neptune and Uranus using EOS from DFT and layering due to phase-transitions in water



The phase diagram of water and the unusual magnetic field of Uranus and Neptune
R. Redmer, T.R. Mattsson, N. Nettelman, and M. French
Icarus, in press, doi:10.1016/j.icarus.2010.08.008

Convective-region geometry as the cause of Uranus' and Neptune's unusual magnetic field
Stanley and Bloxham, Nature **428**, 151 (2004).

Numerical dynamo models of Uranus' and Neptune's magnetic fields
Stanley and Bloxham, Icarus **184**, 556 (2006).

- Planetary structure
  - Molecular
  - Ionic
  - Superionic
  - Core
- Corresponds well to the model of Stanley/Bloxham for magnetic field
- The phase-diagram of water provides a distinct physical reason for the layering

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We study properties of shocked Xenon for fundamental reasons and for applications

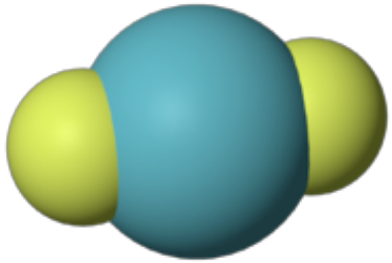
Rich physics

- Transition to metallic liquid
- High melting point under pressure: 163 K at ambient, 3000K at 20-40 GPa
- Propensity for chemical bonds
- Intriguing region of the periodic table
- Xenon is not just another noble gas
- Tamper gas in experiments

33 As	34 Se	35 Br	36 Kr
51 Sb	52 Te	53 I	54 Xe
83 Bi	84 Po	85 At	86 Rn

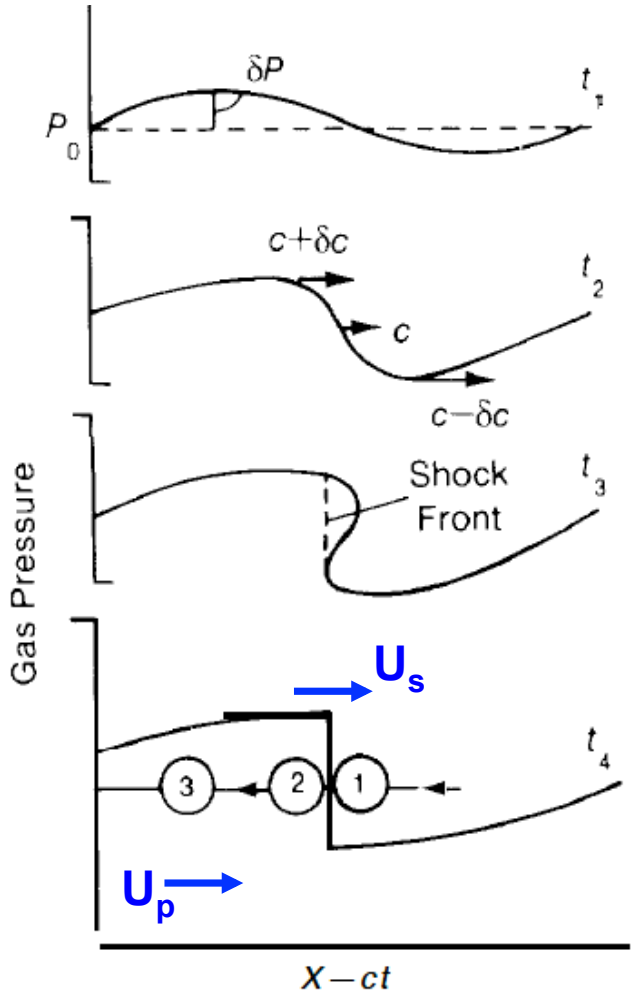
Theoretical/ modeling dimension

- Importance of van der Waals interaction
- Investigate the accuracy of different density functionals
- Assess the accuracy of existing equations of state for Xenon



XeF_2

Shock waves: discontinuity but with a thermodynamic constraint on the equilibrium state after the shock front



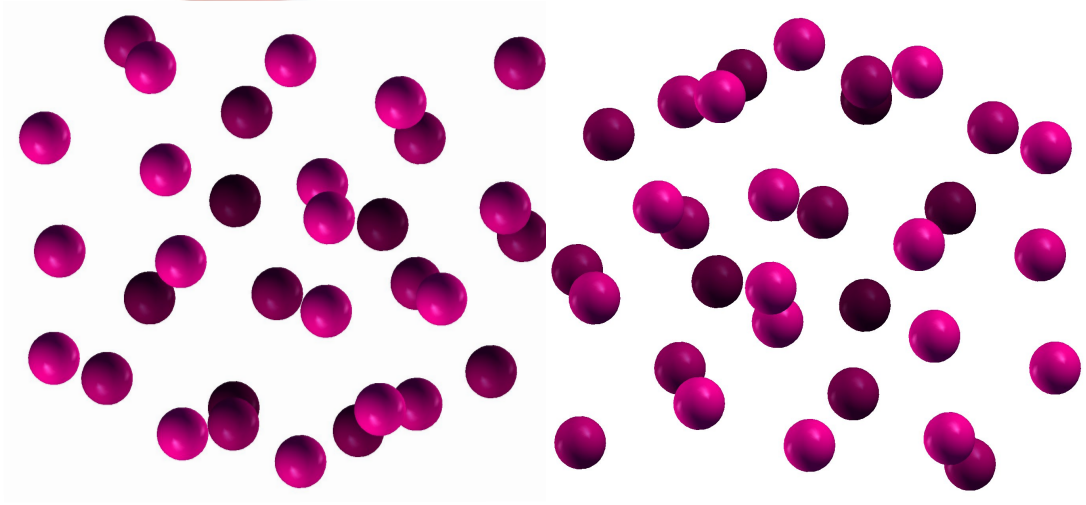
- Density/pressure/nonlinearity dependence of sound speed
- Discontinuity at shock, but a steady traveling wave
- $V_{shock} > V_{sound}$
- *Conservation of mass, energy, and momentum* lead to the Rankine-Hugoniot condition for the initial (1) and final state (2)

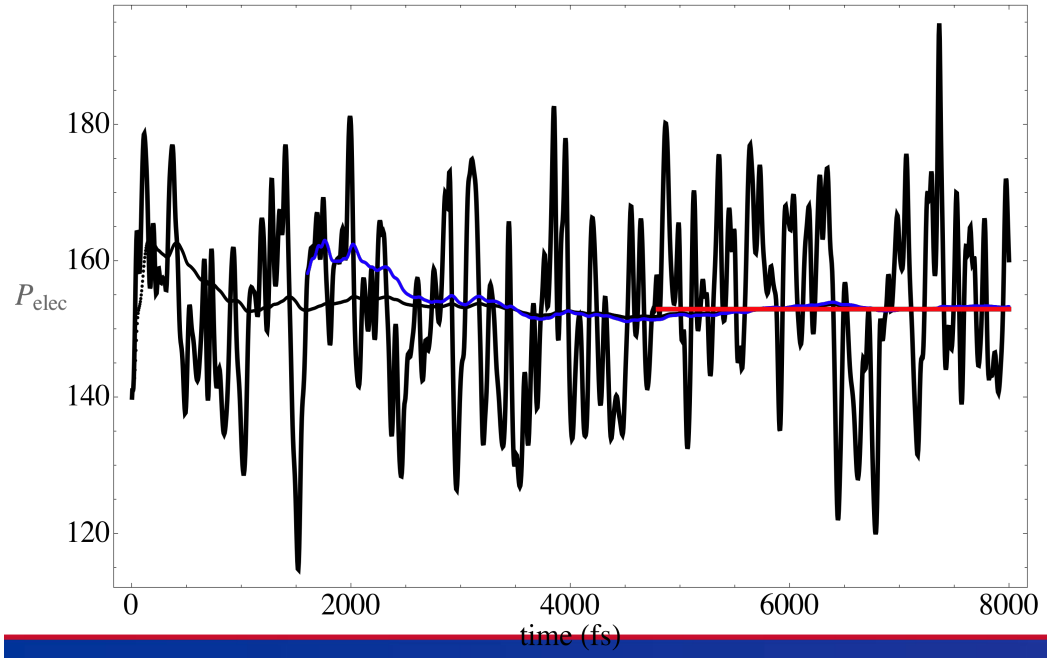
$$2(E_2 - E_1) = (P_2 + P_1)(\upsilon_1 - \upsilon_2)$$

- E - internal energy
- P - pressure
- v – volume

- *Need to calculate thermo-physical properties with high accuracy*

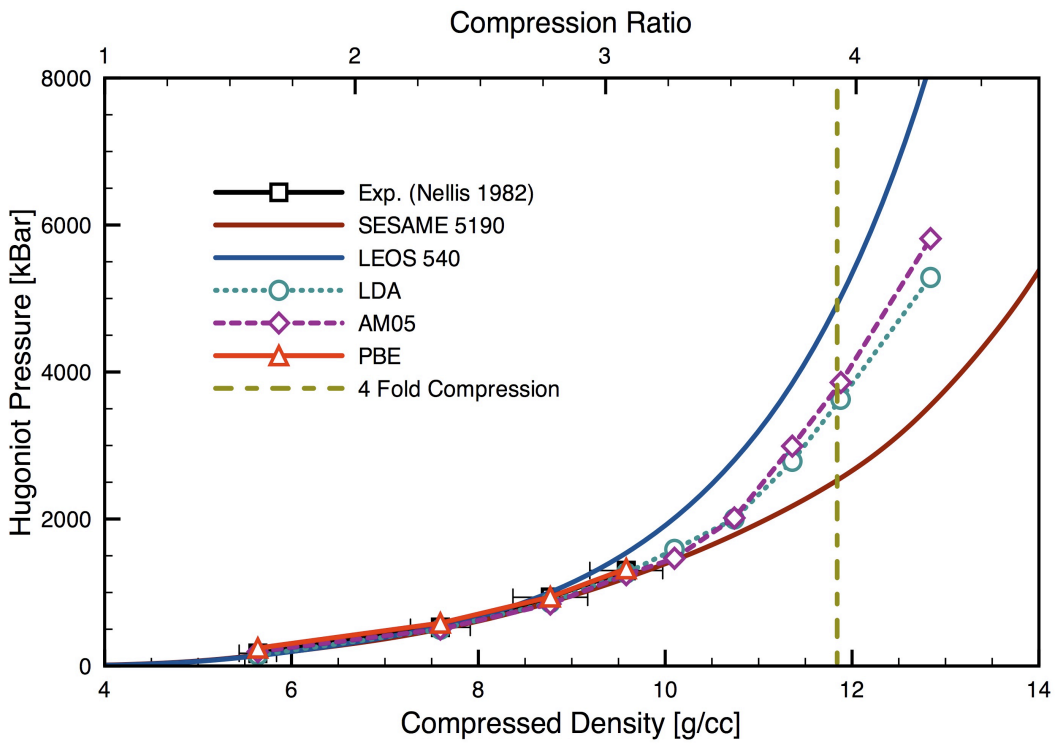
Very narrow range in temperature for the liquid xenon reference state at normal pressure





- Liquid Xenon initial state:
- 2.97 g/cm^3
- 164 +/- 1 K
- Reference value for Hugoniot curve: E_1, P_1
- Long DFT-MD simulations (tens of ps) to reach statistical uncertainty that matches the convergence

DFT predictions of high-pressure Hugoniot for liquid xenon presented at the SCCM meeting in Nashville 2009



SESAME 5190 too soft

LEOS 540 too stiff

We predict 4 Mbar at 4-fold compression (12 g/cm^3)

Significant differences when going beyond the range of existing experiments

Z shock experiments in the multi-Mbar range scheduled

Multi-Mbar shock experiments on Z confirmed the DFT-MD predictions, and go even higher in pressure

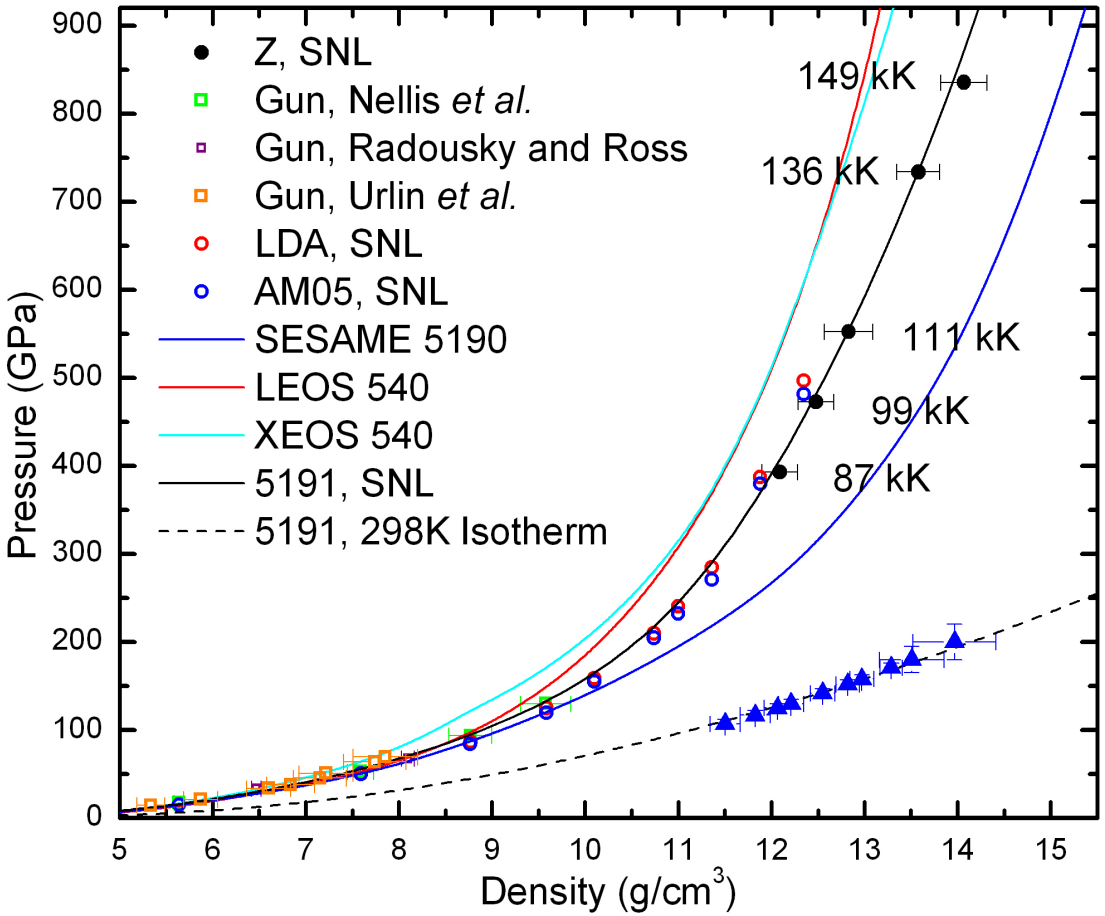
High-precision shock experiments above 8 Mbar

Beyond four-fold compression of liquid xenon (14 g/cm^3)

DFT-LDA and DFT-AM05 in excellent agreement with data

Developed a new wide-range tabular EOS SESAME 5191, it is available at the LANL SESAME database

The fidelity of the DFT calculations reduced the required number of Z shots

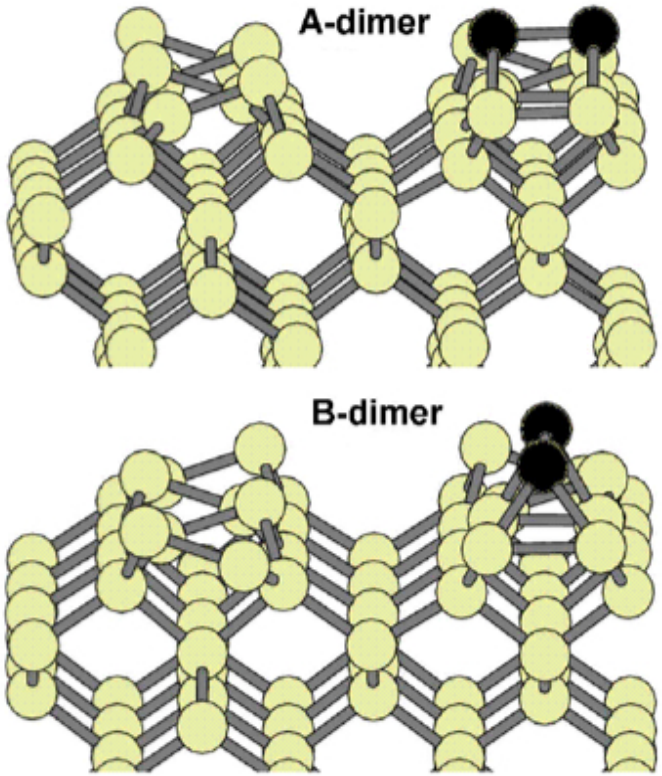


Shock Compression of a Fifth Period Element: Liquid Xenon to 840 GPa, S. Root, R. J. Magyar, J. H. Carpenter, D. L. Hanson, and T. R. Mattsson, Phys. Rev. Lett. **105**, 085501 (2010).

Sandia National Laboratories

Why investigate silicon ad-dimer diffusion on Si(001)?

A-dimer (+0.06 eV)

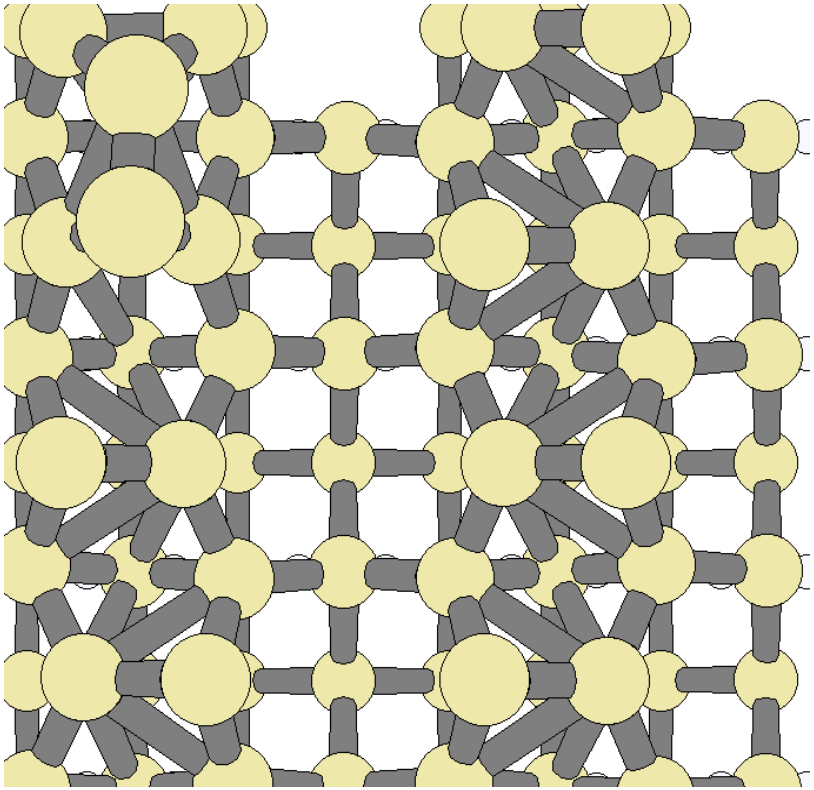


B-dimer is lowest energy state

- Very detailed experimental knowledge of processes at the atomic scale from STM (Brian Swartzentruber at Sandia):
  - Energy of 2 stable configurations
  - Rotation
  - Translation
- Suitable for benchmarking theory and experiments:
  - Verify that we can model diffusion processes and electric fields
- Electric fields:
  - Change surface morphology
  - A condition to change/control in growth
- Si(001) is a model system for semiconductor surfaces and technologically important

Calculated dimer diffusion path 1, Terakura 1996.

- Begins and ends with a B-dimer
- The dimer moves as an entity



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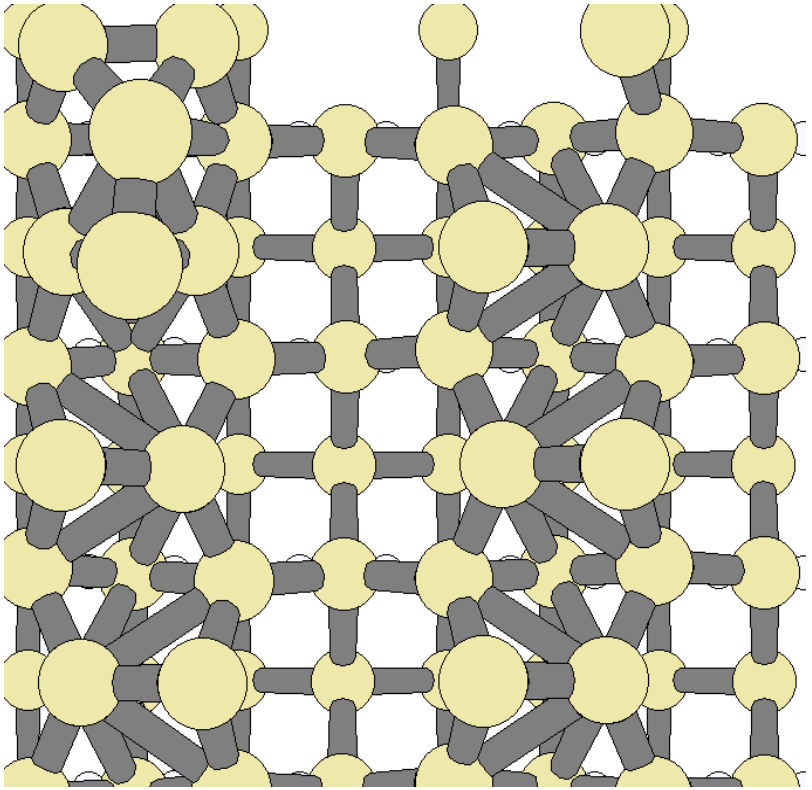

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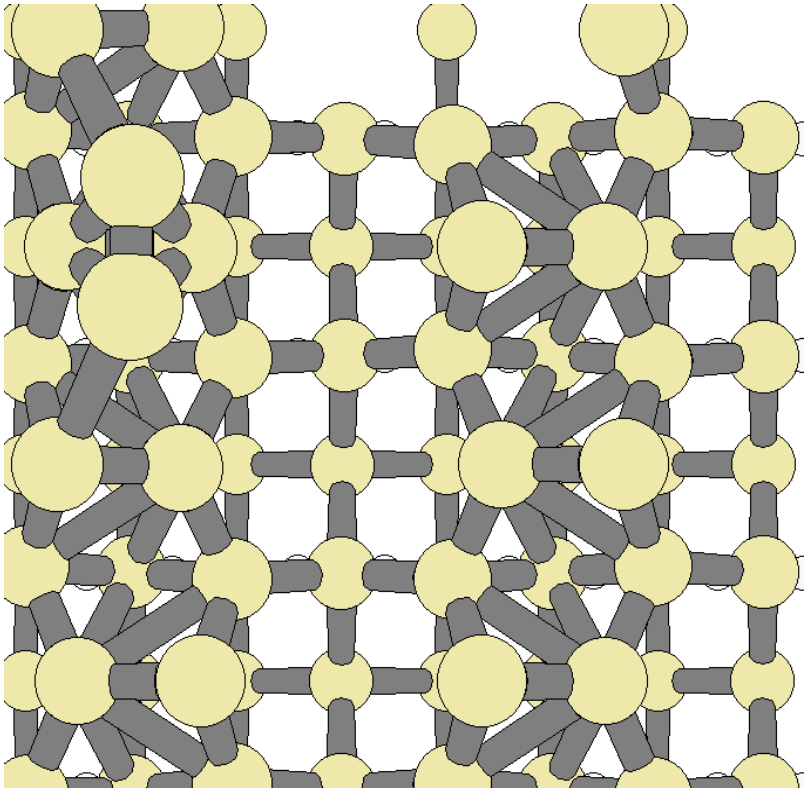

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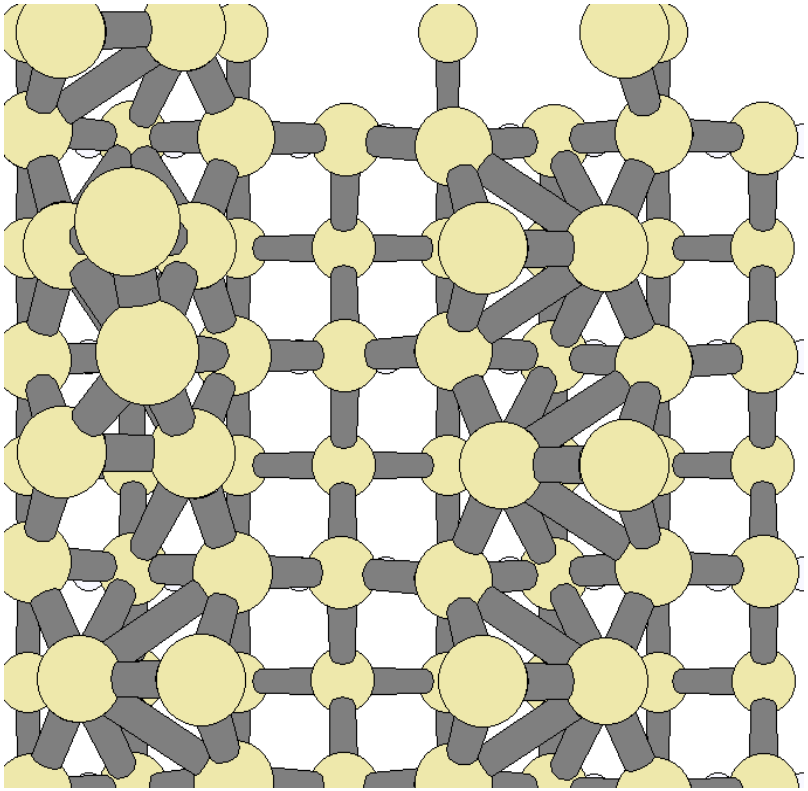

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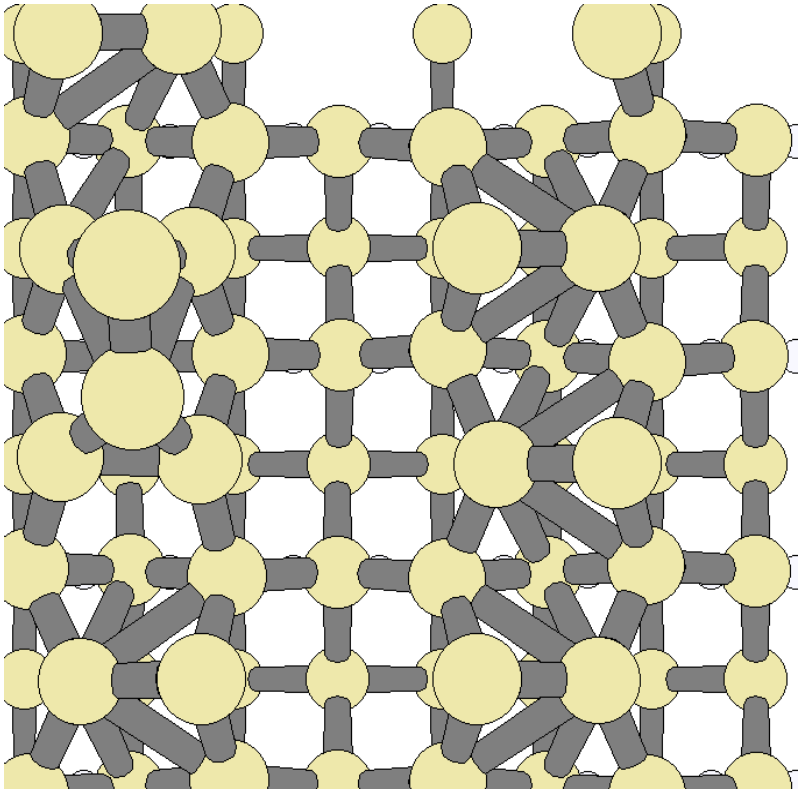
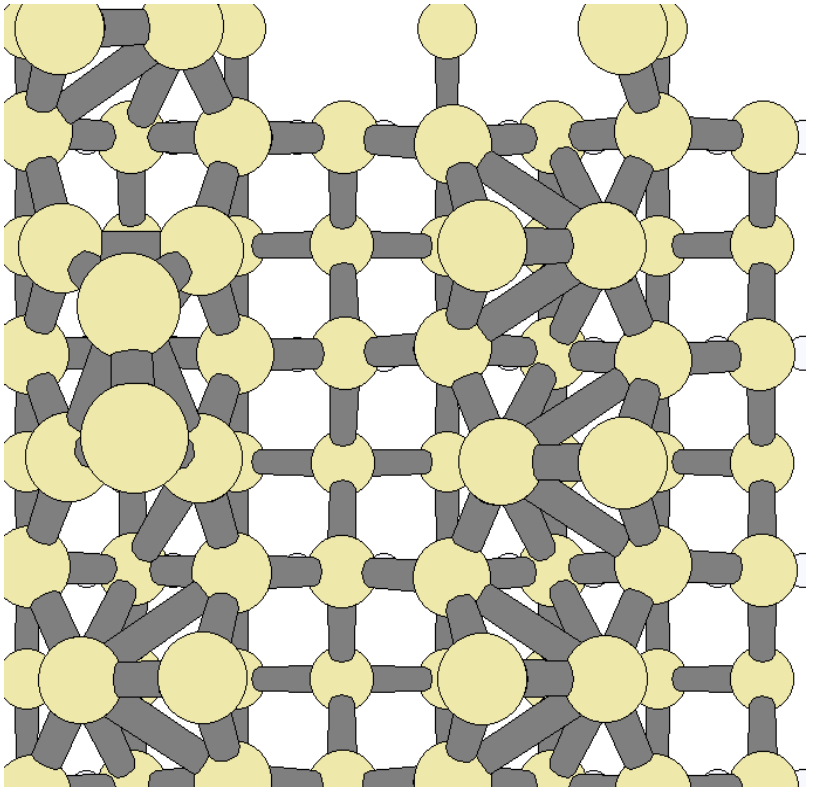


Calculated dimer diffusion path 1, Terakura 1996.

- Begins and ends with a B-dimer
- The dimer moves as an entity
- Barrier 1.44 eV is too high compared to STM data



Si ad-dimer on Si(001) diffusion, making progress on the diffusion mechanism by exploring other ones

- Translation processes:
  - Rule out the straight drag (1.44 eV, too high).
  - Not break-up (1.33 eV is too high, in addition a different diffusion statistics.)
  - Piecewise (next slide).
- Agrees with experimental results.
- Everything seems to work out

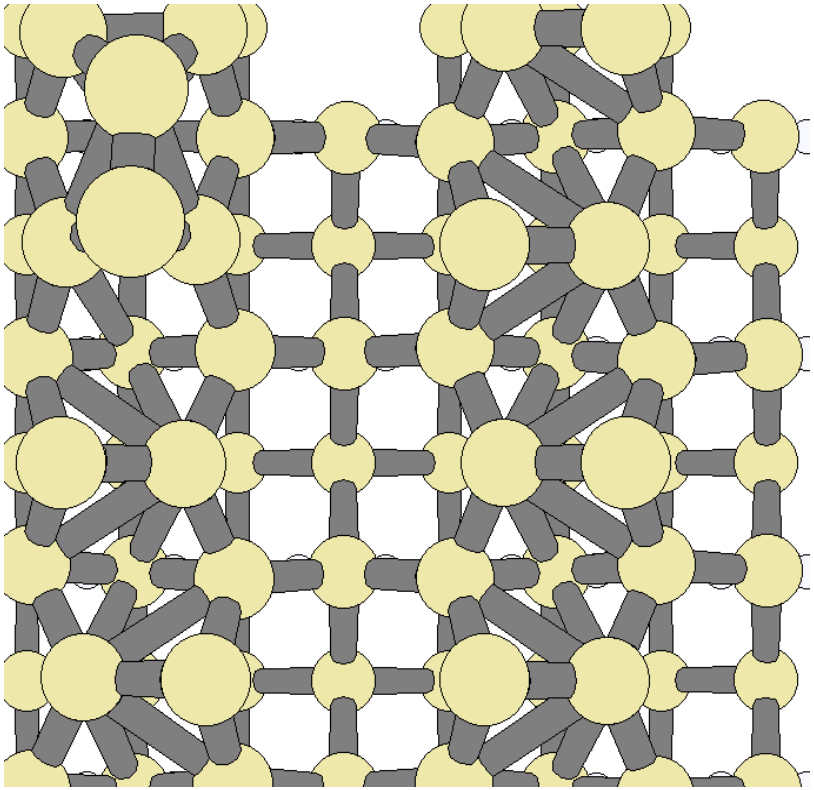
Diffusion (DFT: piecewise mech.)

Group	STM	DFT
Swartzentruber'98	0.94	
Ganz et al. '99	1.09	1.08
Lu et al. '00		1.02
This work		1.14

Electric field effects on surface dynamics: Si ad-dimer diffusion and rotation on Si(001)
T. R. Mattsson, B.S. Swartzentruber, R. Stumpf, and Peter J. Feibelman, Surface Science **536,** 121 (2003).

Piecewise diffusion path, Terakura 1997.

- Begins and ends with a B-dimer.
- The dimer splits into a metastable state.
- Can move back or forward by passing a small barrier.
- About right level of barrier: 1.1 eV.



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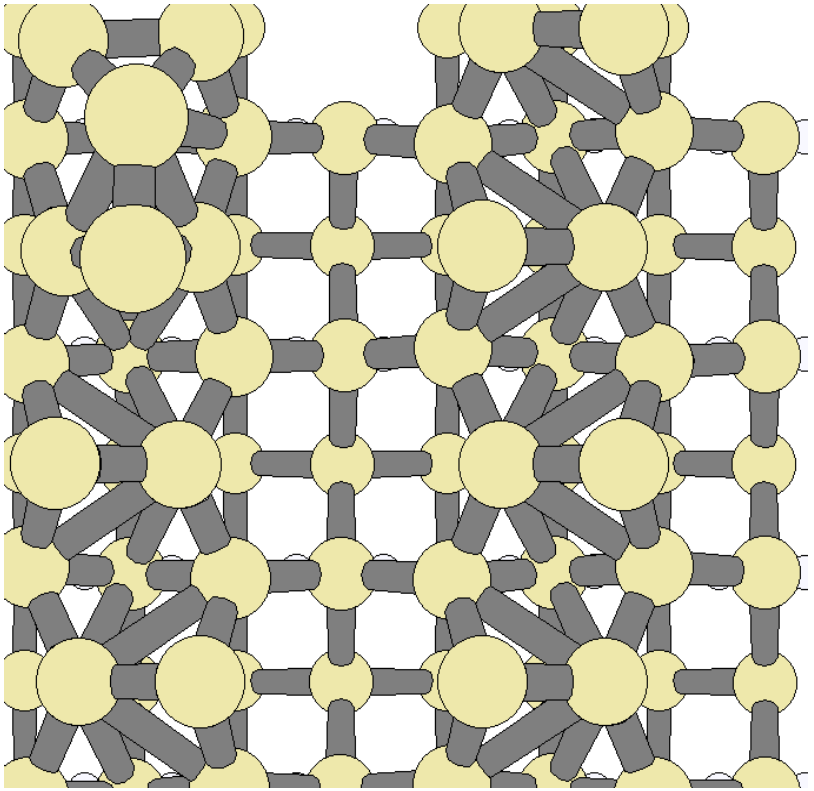

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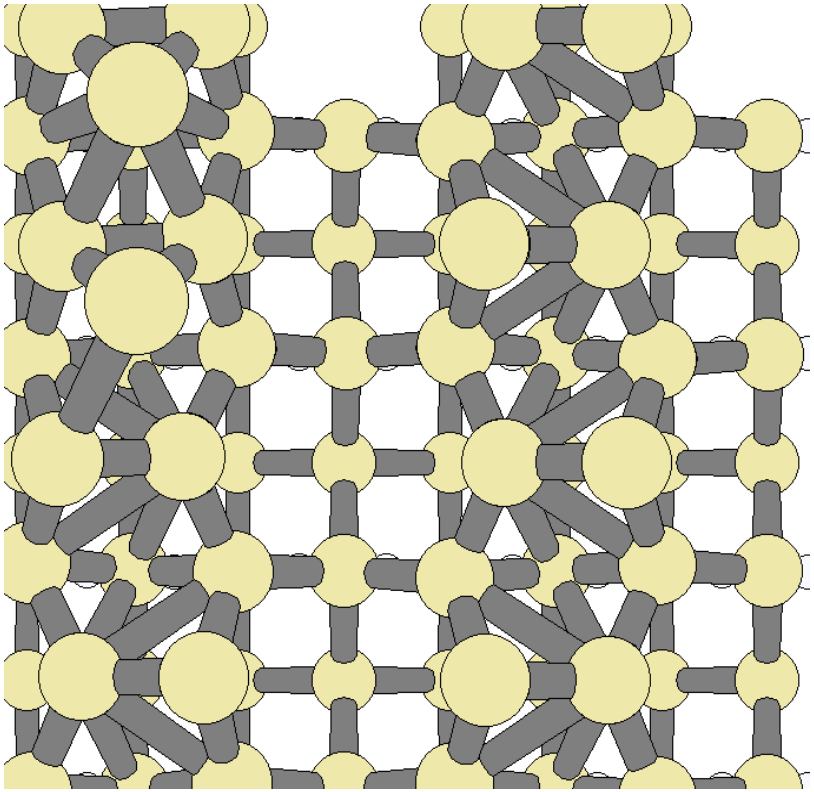

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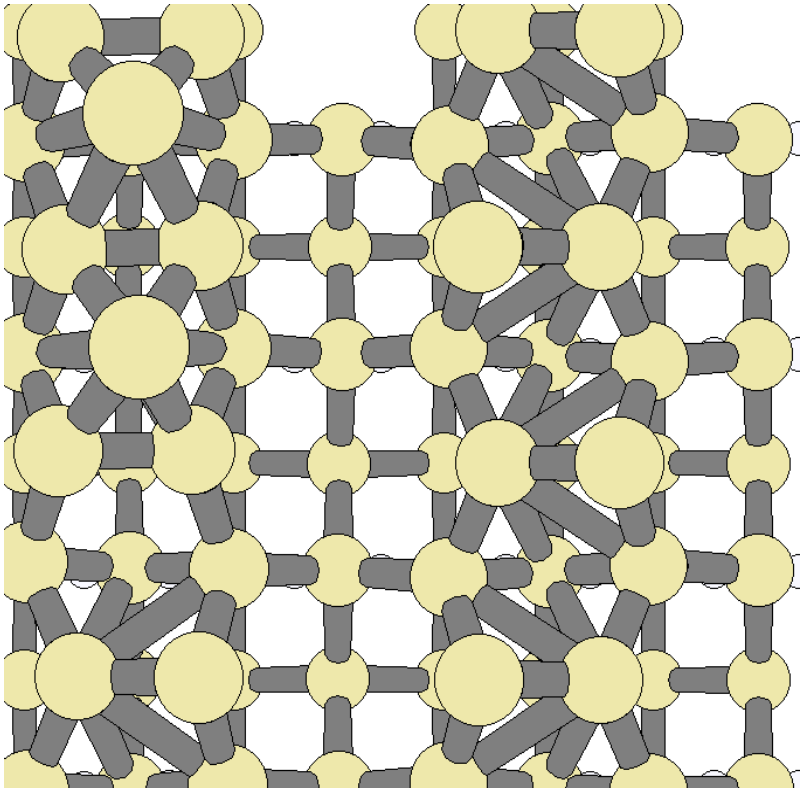

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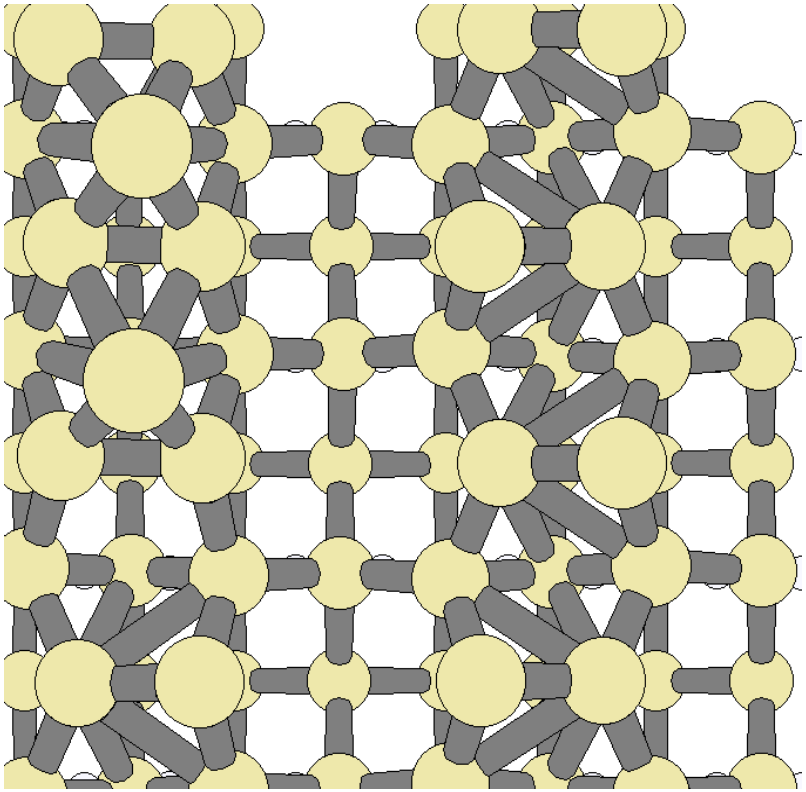

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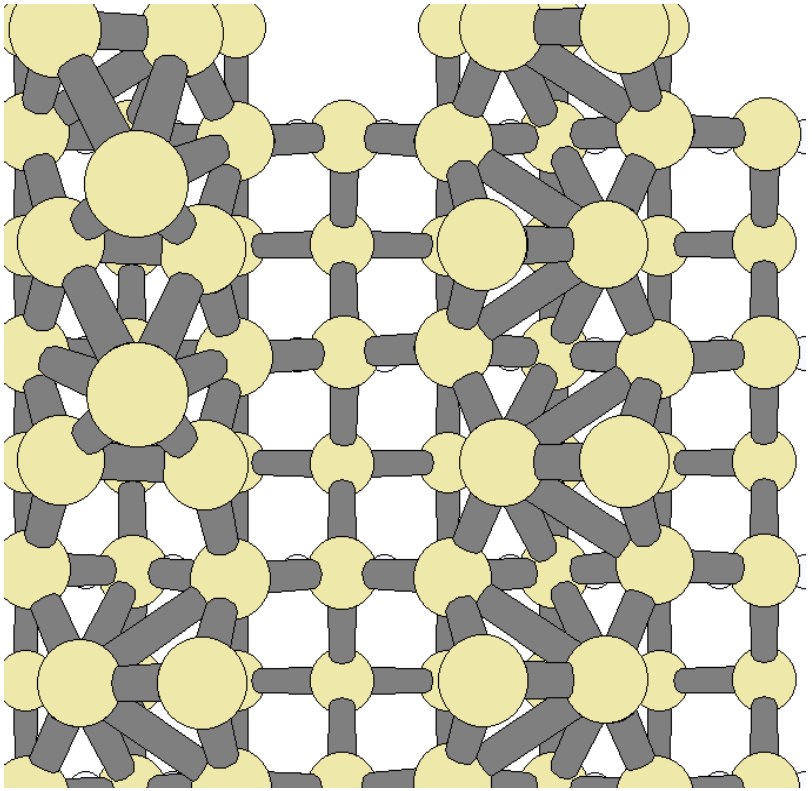

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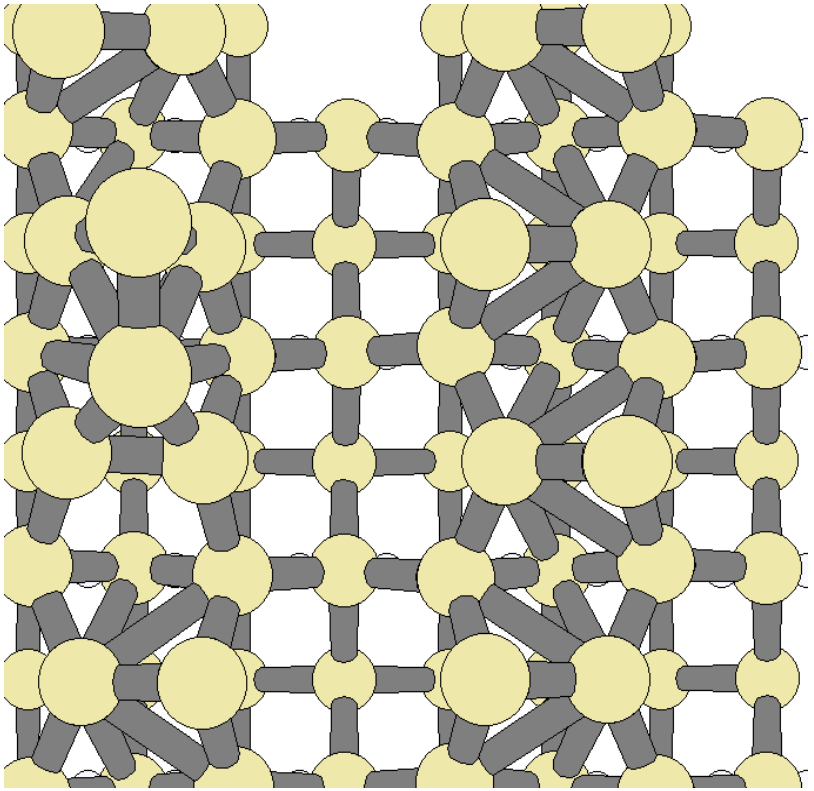

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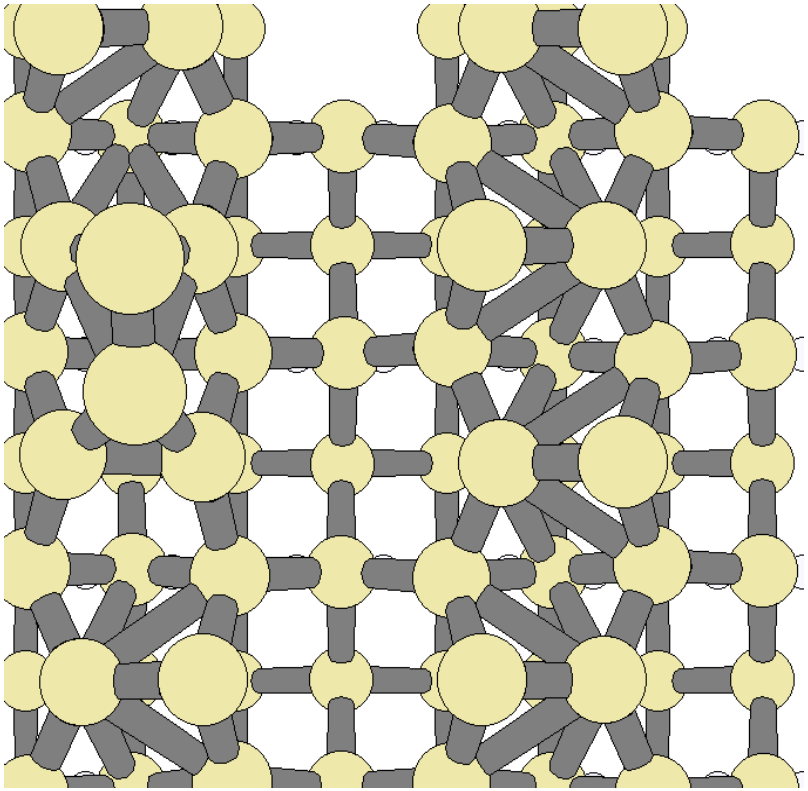

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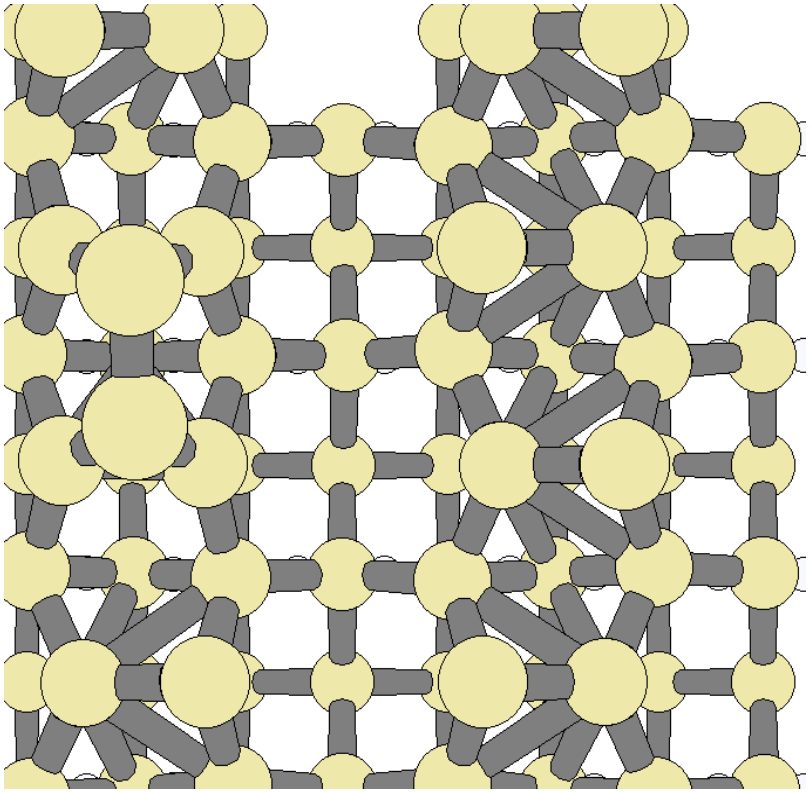

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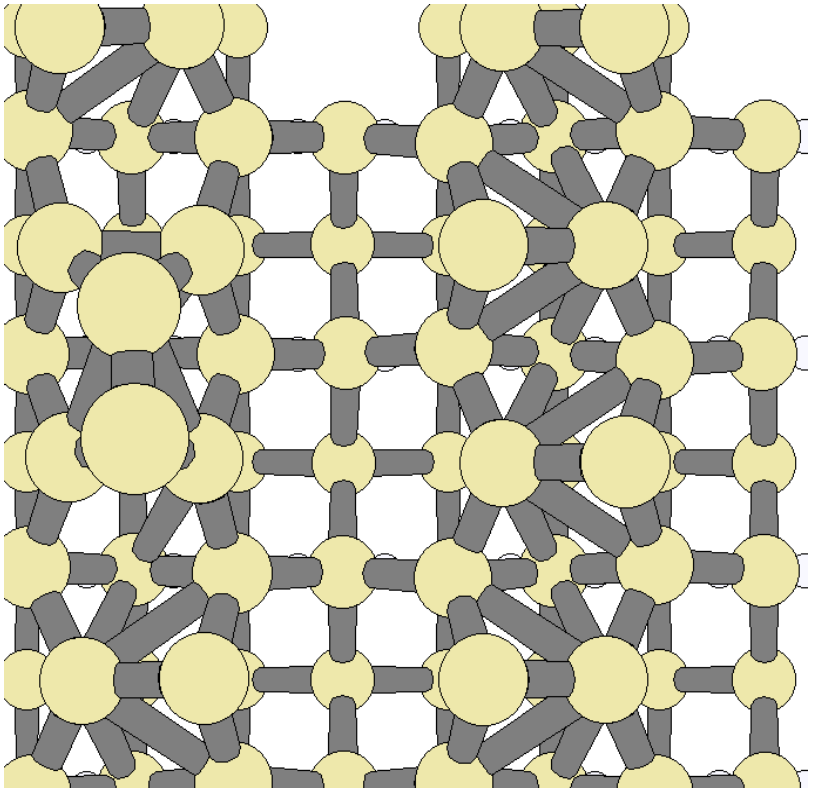
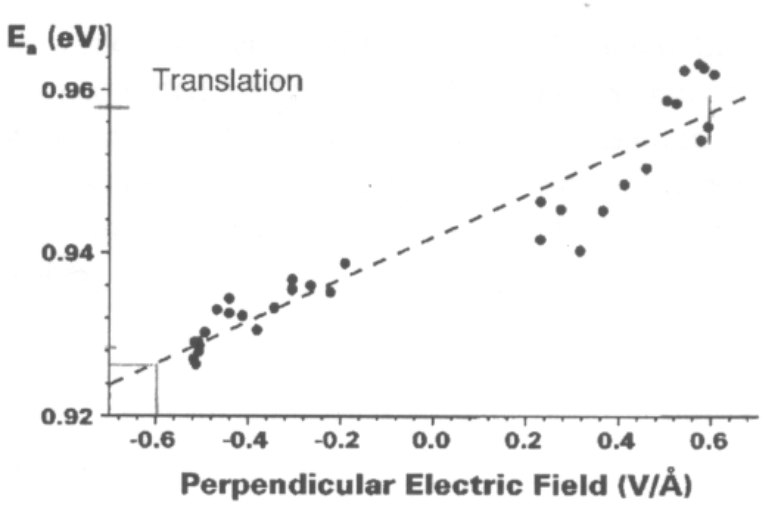
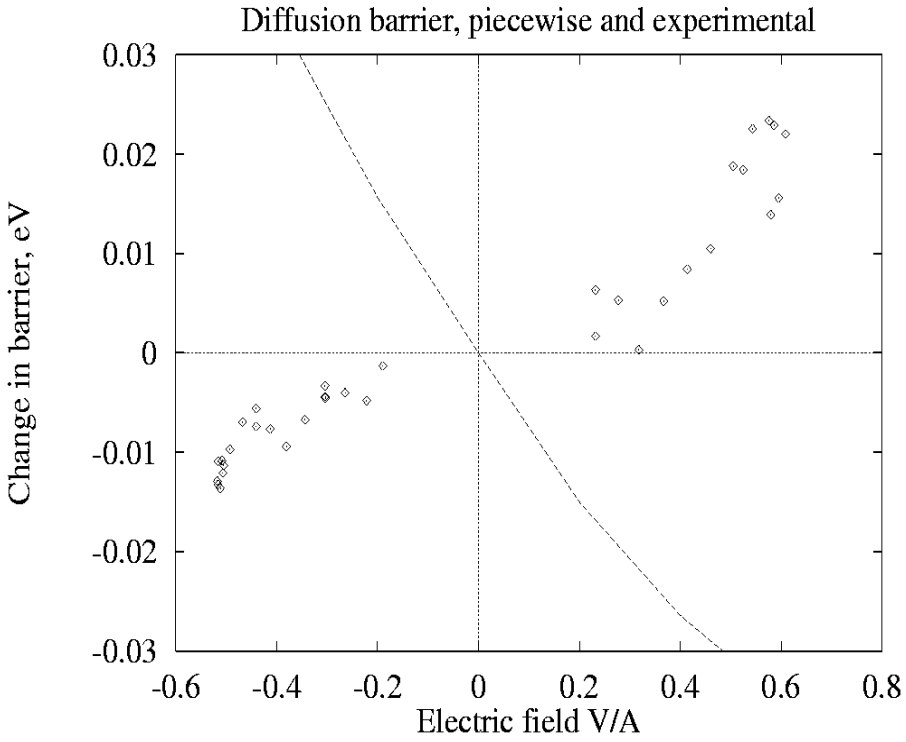
- *Looks very promising*



Si ad-dimer on Si(001), electric field.



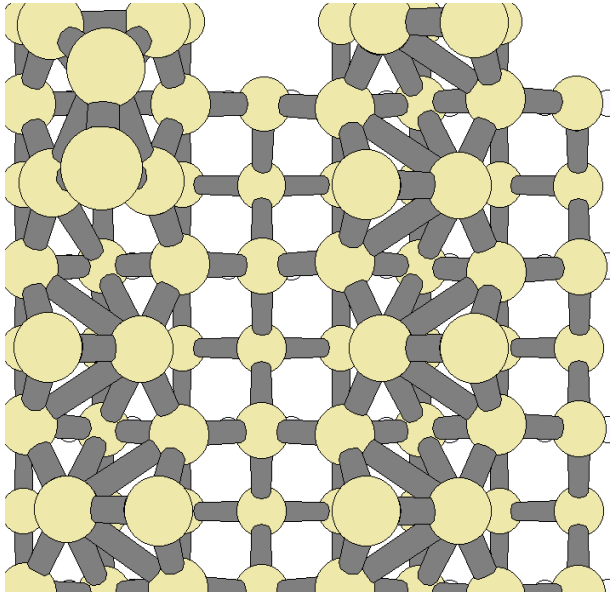
Direct measurement of field effects on surface diffusion, J. M. Carpinelli and B.S. Swartzentruber, Phys. Rev. B **58**, 13423 (1998).



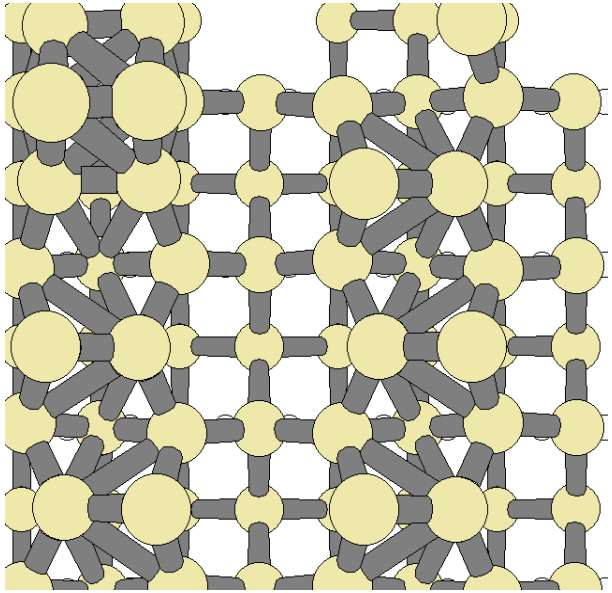
Our calculations yield opposite field dependence to experiments for the piece-wise diffusion mechanism.

Si ad-dimer on Si(001)

B-dimer



A-dimer (+0.06 eV)



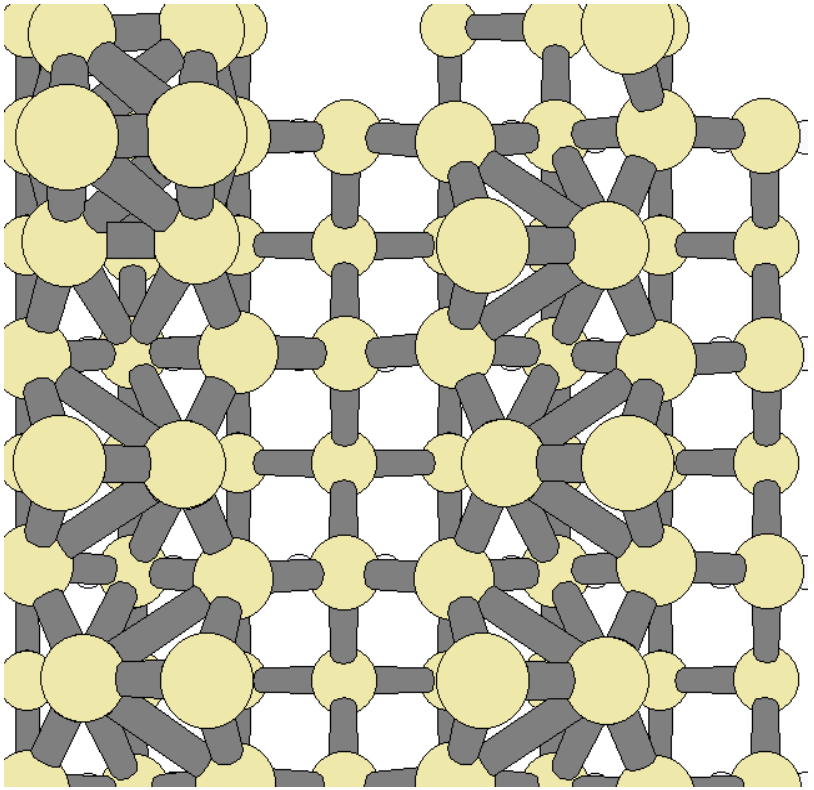
$\mathrm{Exp}(-0.06/k_B T_{exp}) = 0.15$

Focusing on the B state is not enough!

Searched for processes using a variety of methods, e.g. nudged elastic band and directed dimer

Walking diffusion path, 2002.

- Begins and ends with an A-dimer!
- The dimer moves as an entity.
- Keeps short bonds to one substrate atom.
- Rotational as well as translational motion.



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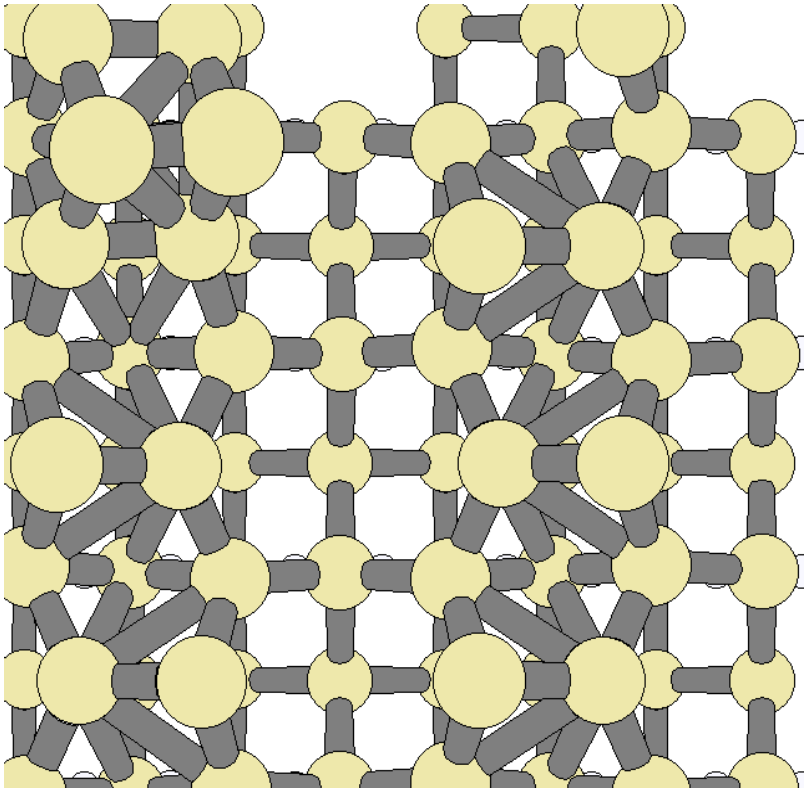

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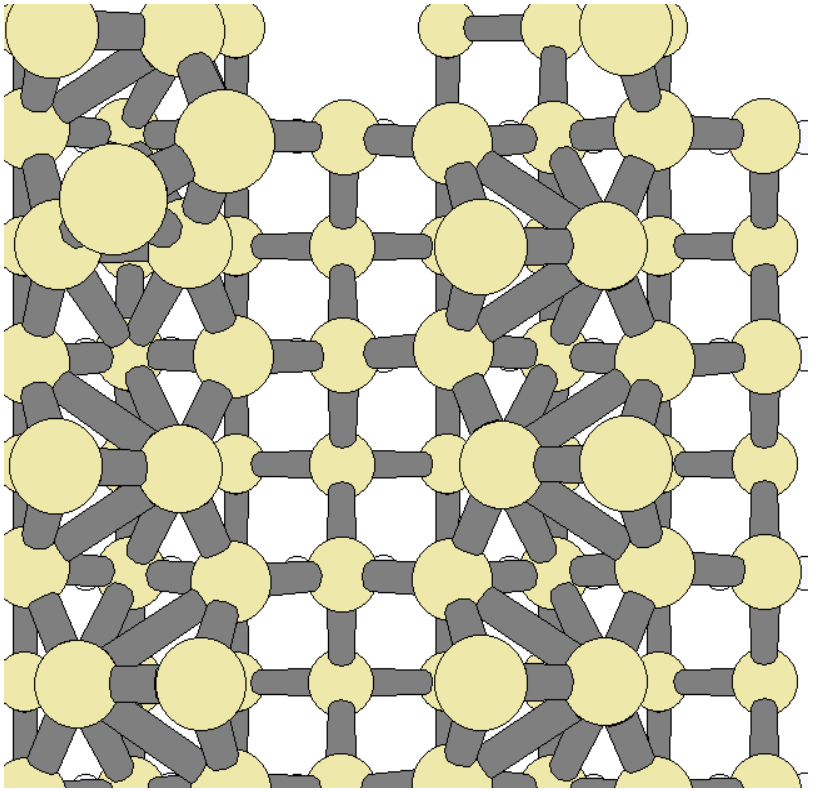

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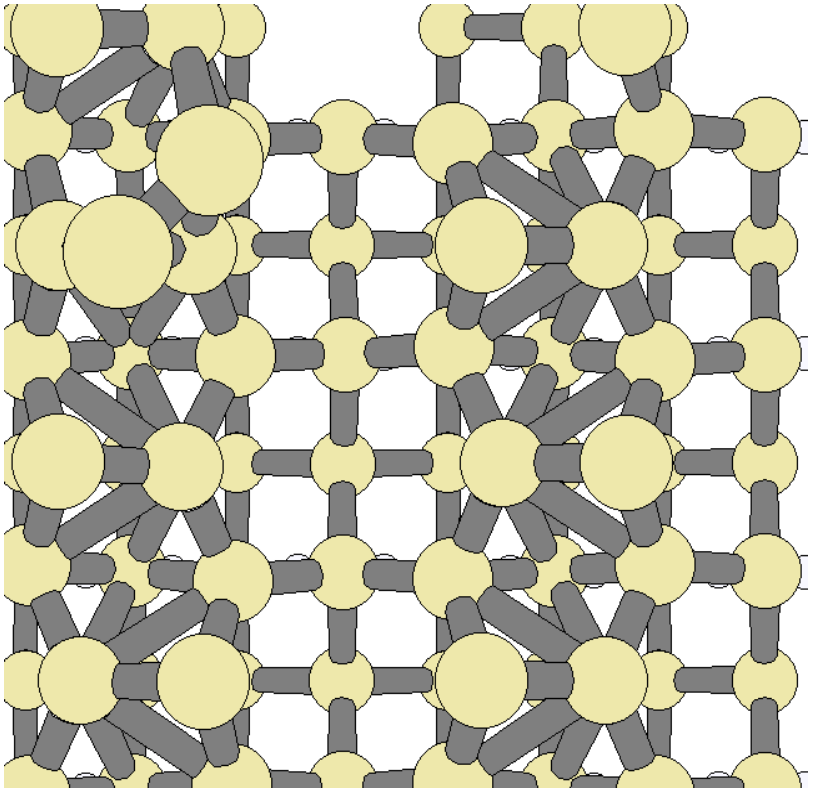

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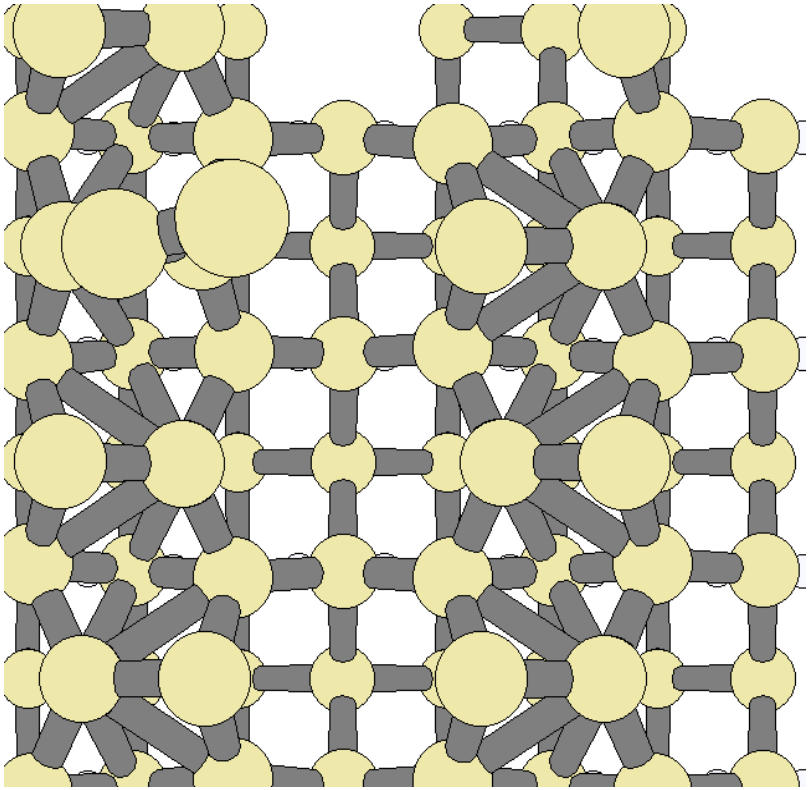

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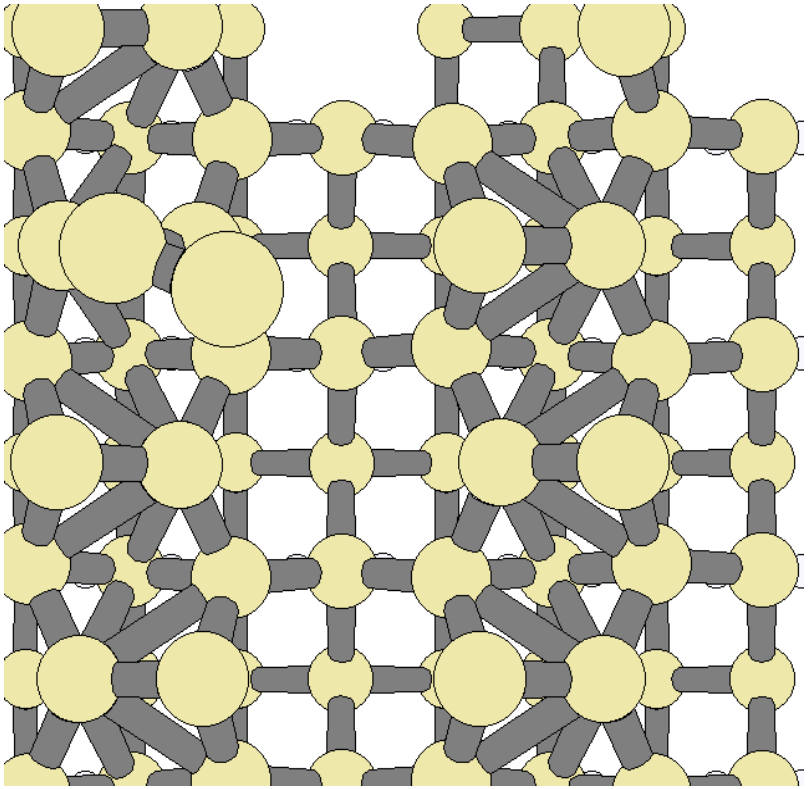

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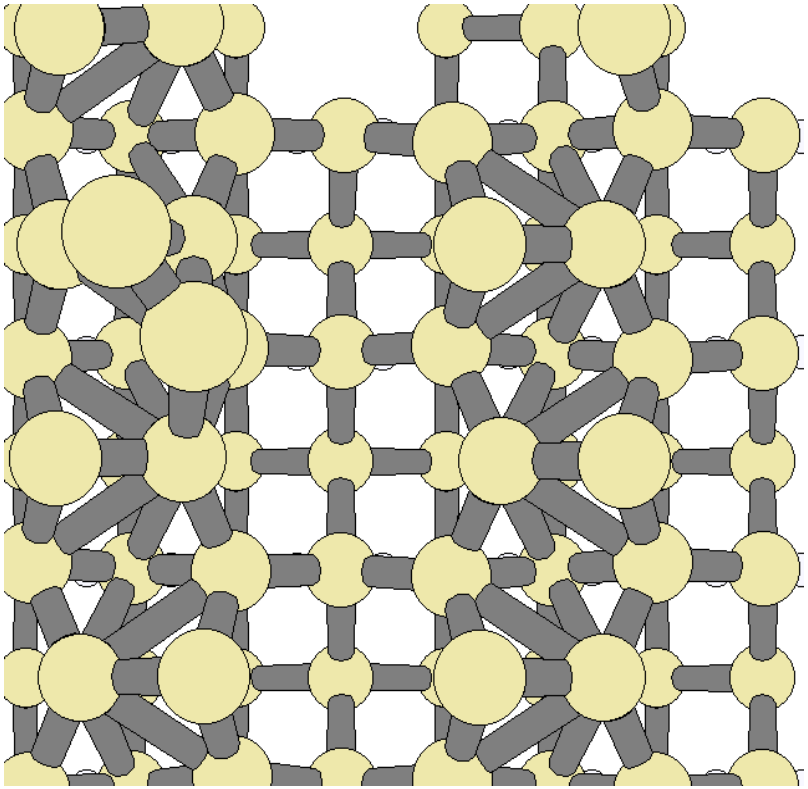

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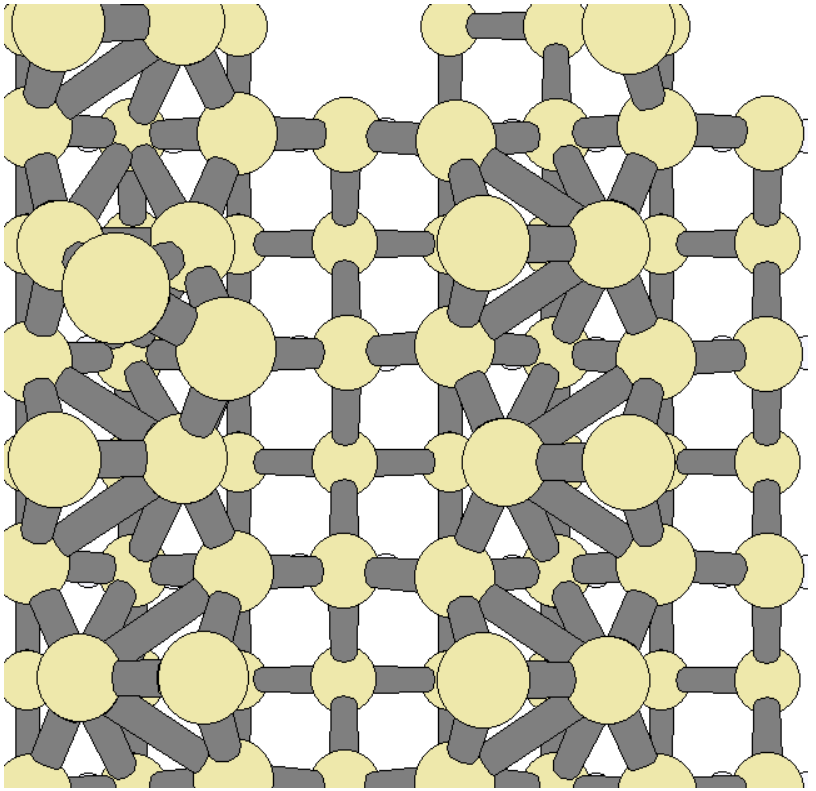

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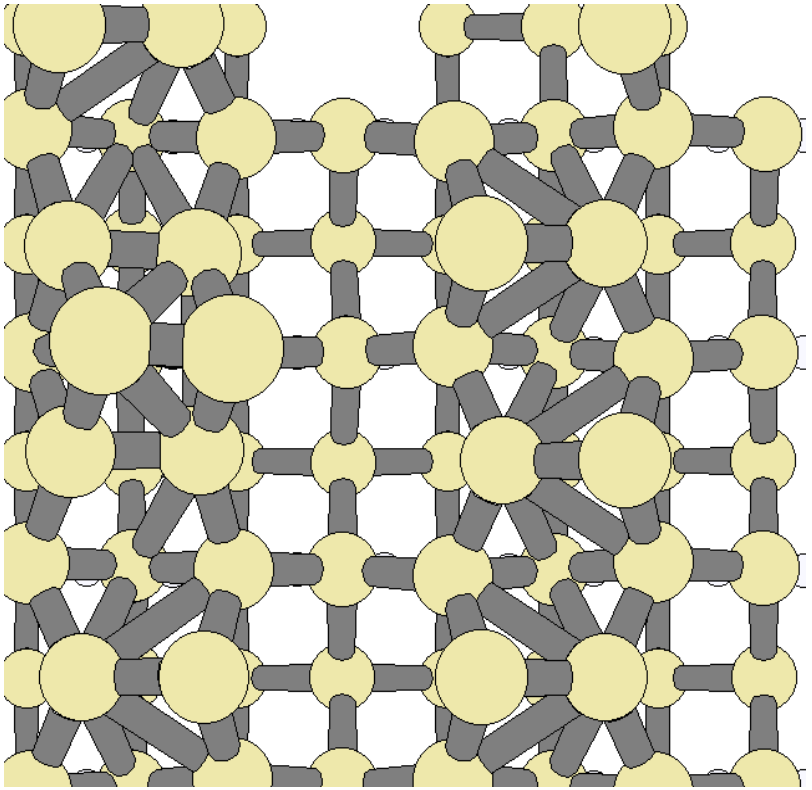

Walking diffusion path, 2002.

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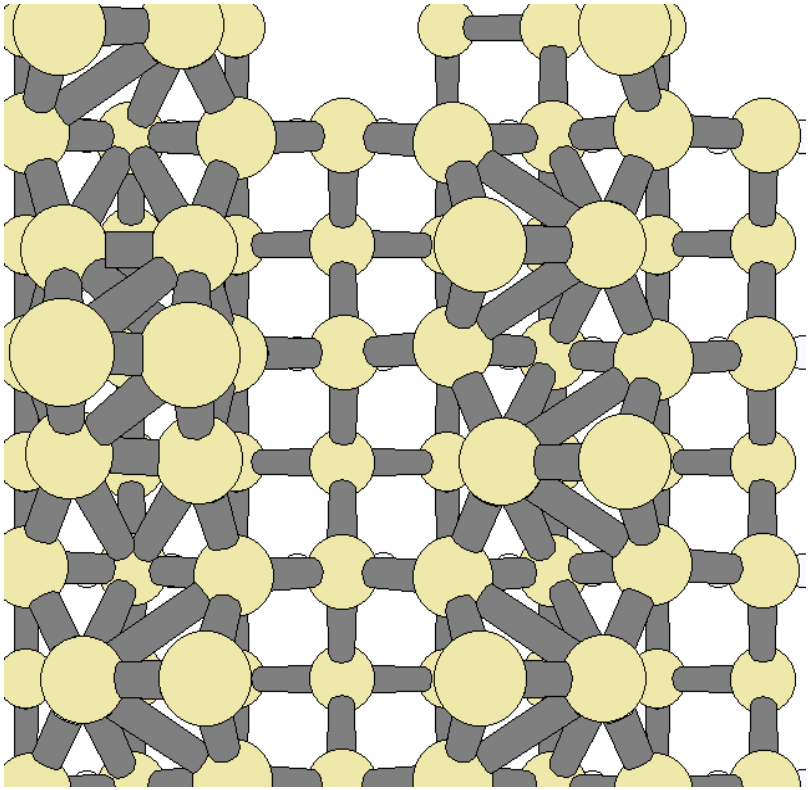
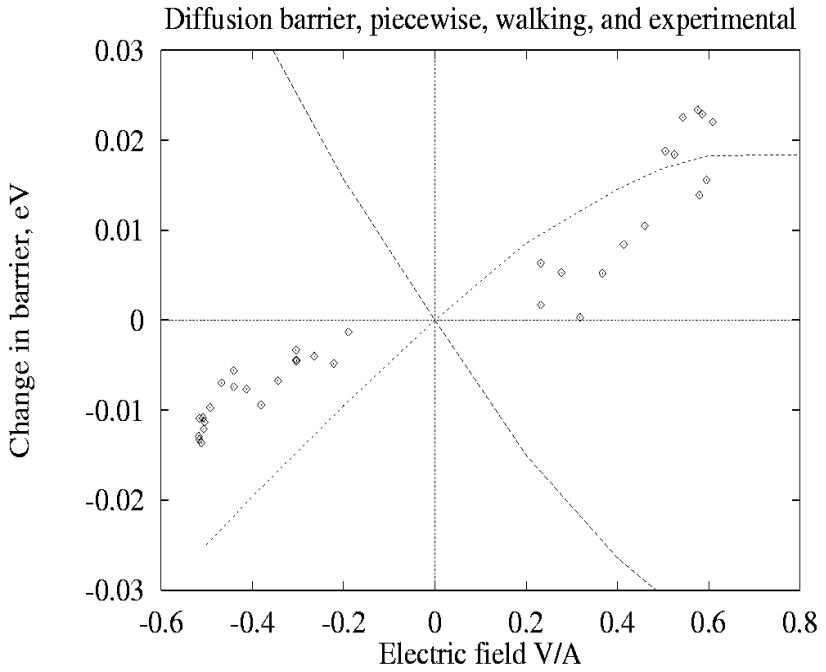
- Rotational as well as translational motion.

- *Walking barrier of 1.04 eV, which is 0.1 eV lower than piece-wise mechanism*



The field dependence is correct for the "walking" diffusion mechanism, barrier increasing with field

- The field-dependence is OK
- *We have found a promising candidate for the diffusion mechanism*
- It is possible to change the diffusion mechanism by applying a field



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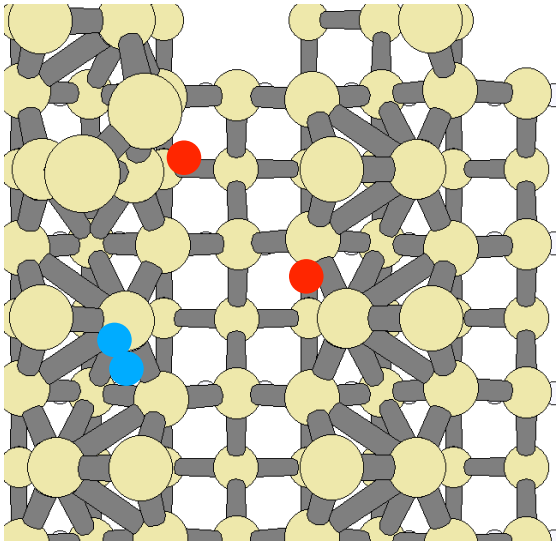
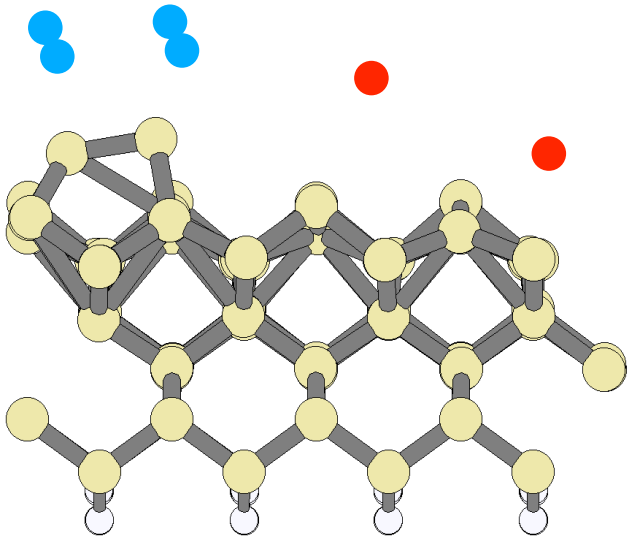
T. R. Mattsson, B.S. Swartzentruber, R. Stumpf, and Peter J. Feibelman, Surface Science **536,** 121 (2003).

Changing the Diffusion Mechanism of Ge-Si Dimers on Si(001) using an Electric Field
L. M. Sanders, R. Stumpf, T. R. Mattsson, and B. S. Swartzentruber, Phys. Rev. Lett. ***91,*** *206104 (2003).*

Considerations for modeling processes at semiconductor surfaces : trade-off between size/time and fidelity





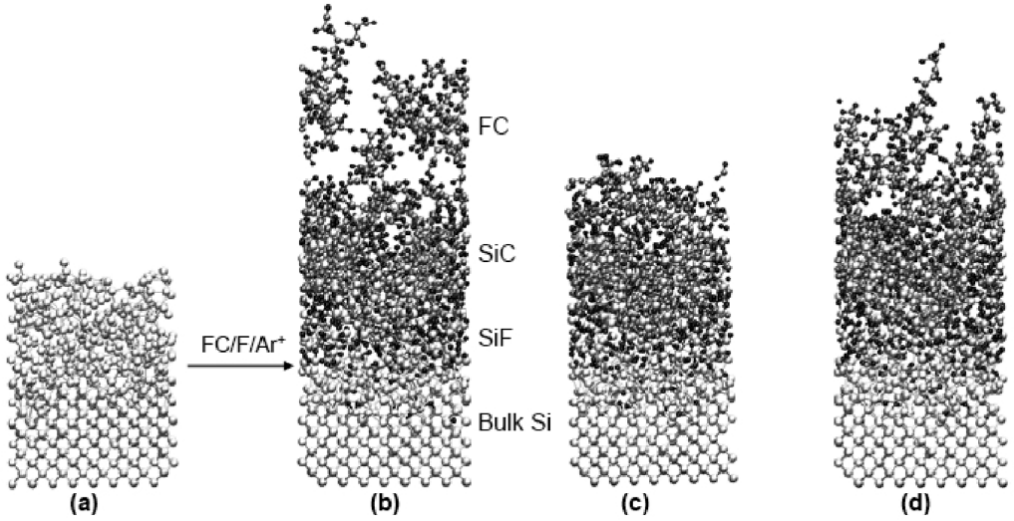
- Investigate equilibrium/ thermodynamics
- Investigate kinetics/ processes
- Identify appropriate length- and time- scales

- DFT – best possible interactions but limited to 100-200 atoms
- Can investigate elemental processes for surface reactions, etching, sputtering, etc.

Considerations for modeling processes at semiconductor surfaces : trade-off between size/time and fidelity

D. B. Graves and P. Brault, J. Phys. D: Appl. Phys. **42**, 194011 (2009).

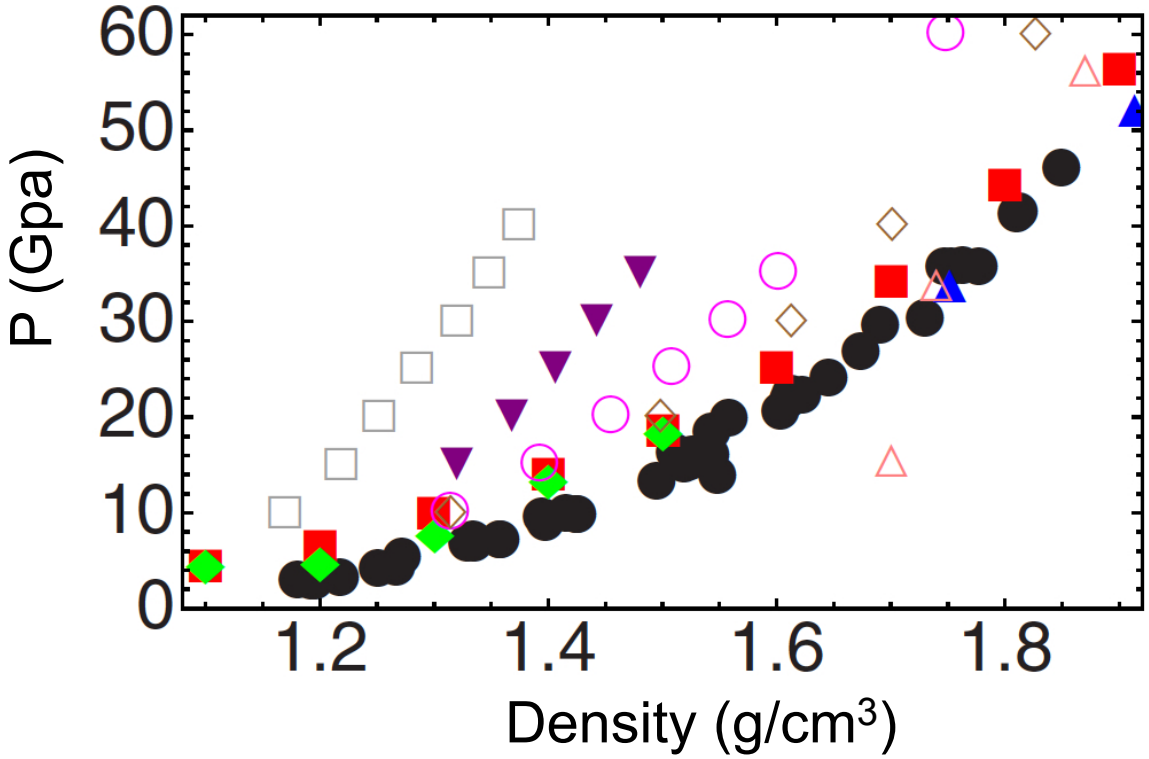
Modeling Si etch with fluorocarbon neutrals and argon ions using Tersoff-Brenner style REBO potential.



- Model potentials
- Can investigate several ns of time and tens of thousands of atoms
- *The fidelity of the model potential is the limiting factor*

Benchmarking four model potentials for hydrocarbons under shock compression

Shocked polyethylene



Tight-binding (J.D Kress et al SCCM 1999)
AIREBO
OPLS
Borodin-Smith (exp6)
ReaxxFF
DFT-AM05
Data (Nellis/ LASL handbook)

Comparing different model potentials for shocked hydrocarbons.

Temperature range here is relatively limited and relevant to a lot of processing conditions

$300 < T < 2500$ K

First-principles and classical molecular dynamics simulation of shocked polymers. T.R. Mattsson et al. Phys. Rev. B **81**, 054103 (2010).

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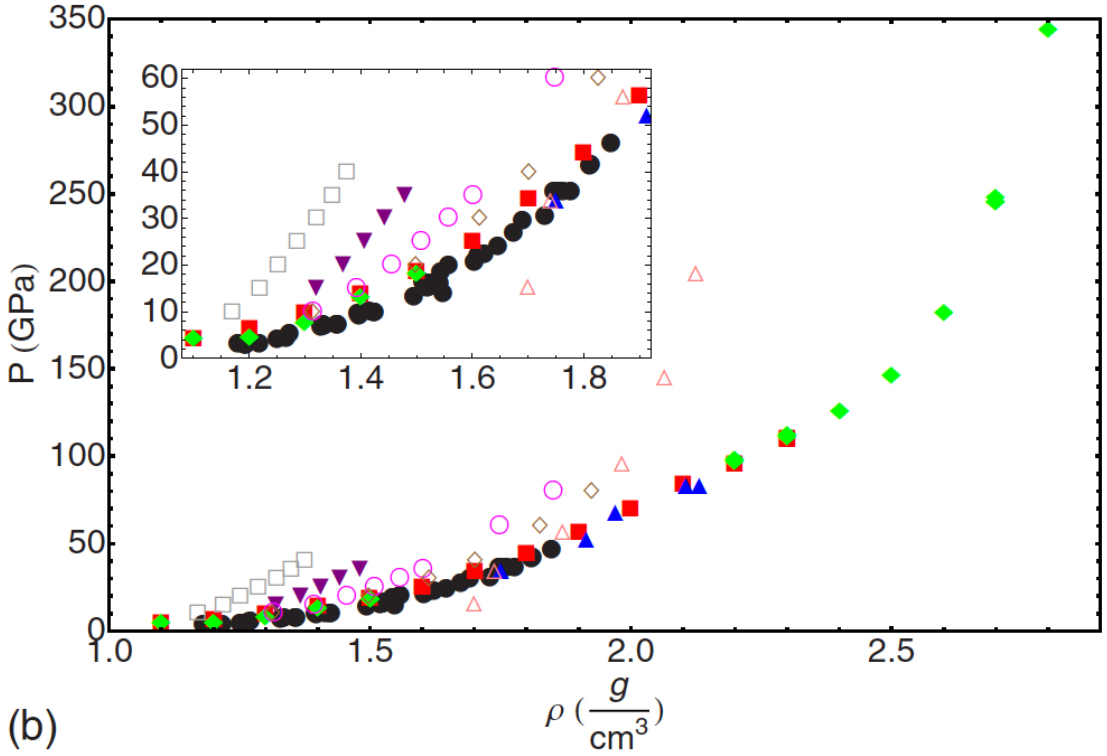
Benchmarking four model potentials for hydrocarbons under shock compression

Shocked polyethylene



(b)

- Tight-binding (J.D Kress et al SCCM 1999)
- AIREBO
- OPLS
- Borodin-Smith (exp6)
- ReaxxFF
- DFT-AM05
- Data (Nellis/ LASL handbook)

Comparing different model potentials for shocked hydrocarbons.

For applications in HEDP and ICF we are interested in Mbar pressures

First-principles and classical molecular dynamics simulation of shocked polymers. T.R. Mattsson et al. Phys. Rev. B **81**, 054103 (2010).

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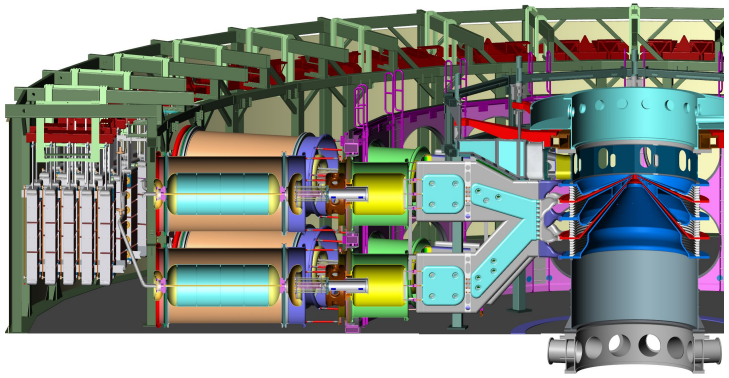
First-principles simulations are key to improving our understanding of materials science and HEDP

- Summary
  - DFT provides insights and data that are very difficult to obtain otherwise.
- Enabling impact on HED modeling
  - Several DFT based materials models are *in daily use* at SNL and elsewhere
  - Direct DFT simulations helps design and analyze experiments
  - Contribute quantitative results for materials science and planetary science



First-principles simulations are now indispensable elements of many types of projects at Sandia.

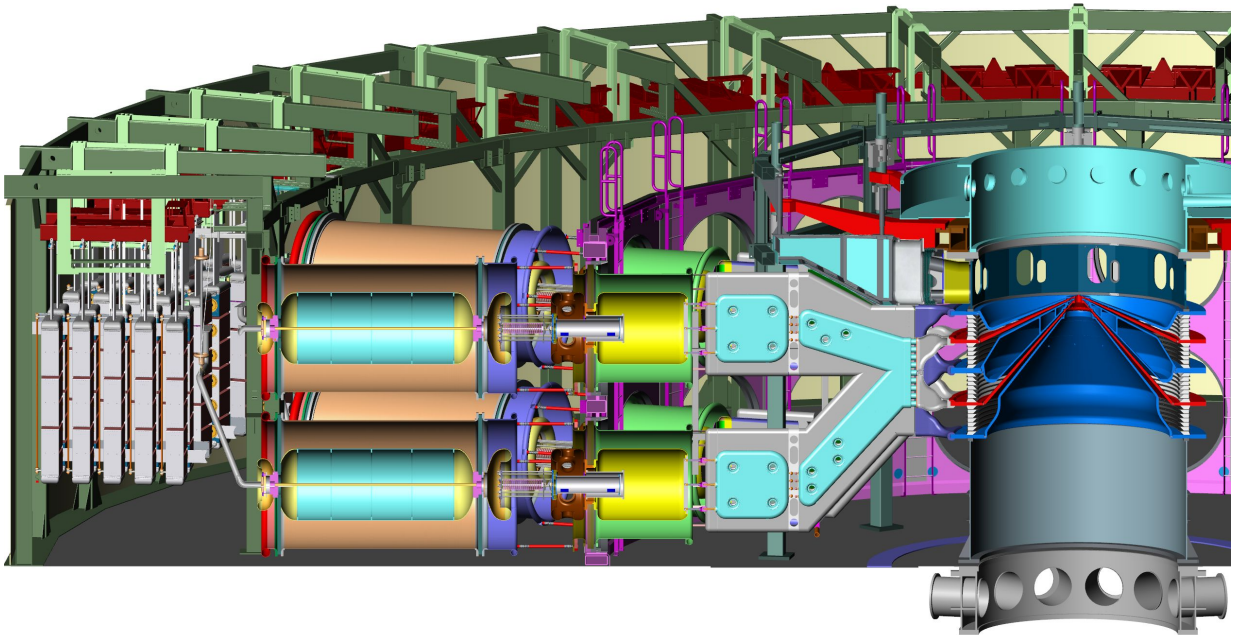
Acknowledgments

Michael Desjarlais for many discussions on HEDP and shock physic as well as introducing me to these topics in 2003

Ann Mattsson for many discussions on DFT and mathematical physics

Tom Mehlhorn and Dawn Flicker for strong support of our work

Ronald Redmer, and students Martin French, Bastian Holst, Andre Kietzmann, Winfried Lorenzen, and Nadine Nettelman for fruitful collaborations and *the planetary modeling slides presented in the talk*



First-principles simulations are now indispensable elements of many types of projects at Sandia.

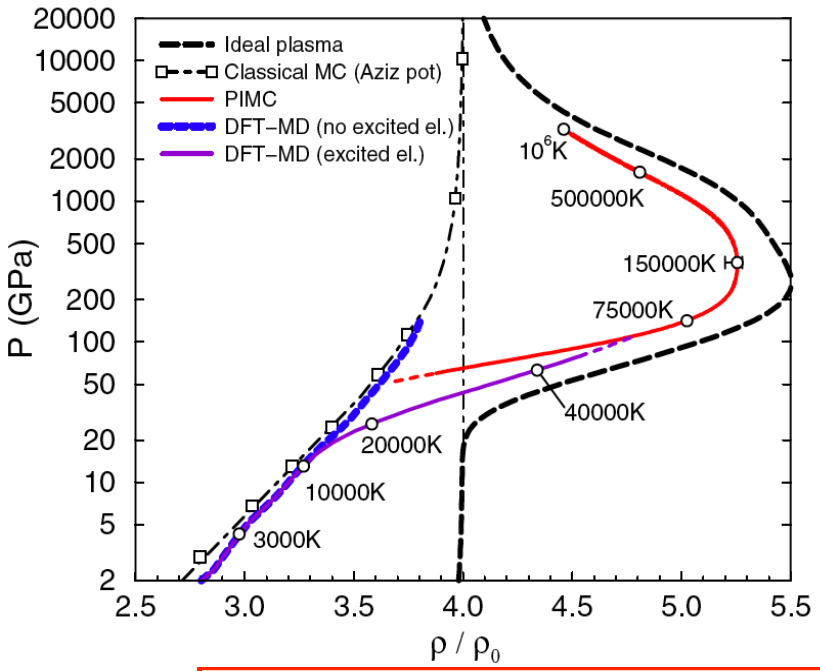
PIMC results for He compares very well to finite-temperature DFT calculations

Shock wave →

E,V,P	E_0,V_0,P_0

Rankine-Hugoniot condition for a single shock relates changes in pressure, volume and energy.

$$H = E - E_0 + \tfrac{1}{2}(V - V_0)(p + p_0) = 0.$$



- PIMC approaches ideal plasma at 10^6 K
- FT-DFT approaches PIMC results.
- Deviations from ground state DFT (Car-Parrinello) as temperature increases.
- Classical MC results deviate too, no electronic degrees of freedom.

B. Militzer Phys. Rev. Lett 97, 175501 (October 2006).

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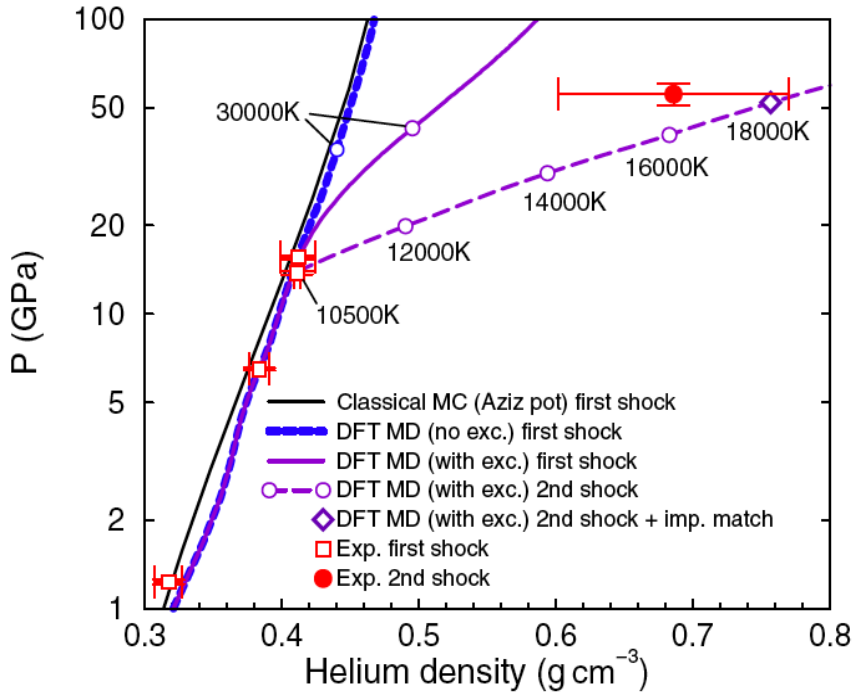
Available (few) experimental results agree with finite-temperature DFT

2nd shock → **1st shock** →

E_2,V_2,P_2 | E,V,P | E_0,V_0,P_0



- Shock experiments probe only certain regions of the phase-diagram.
- FT-DFT captures both first- and second shock data.
- Simulations can go outside the area where experimental data is available -- perhaps even impossible to obtain.

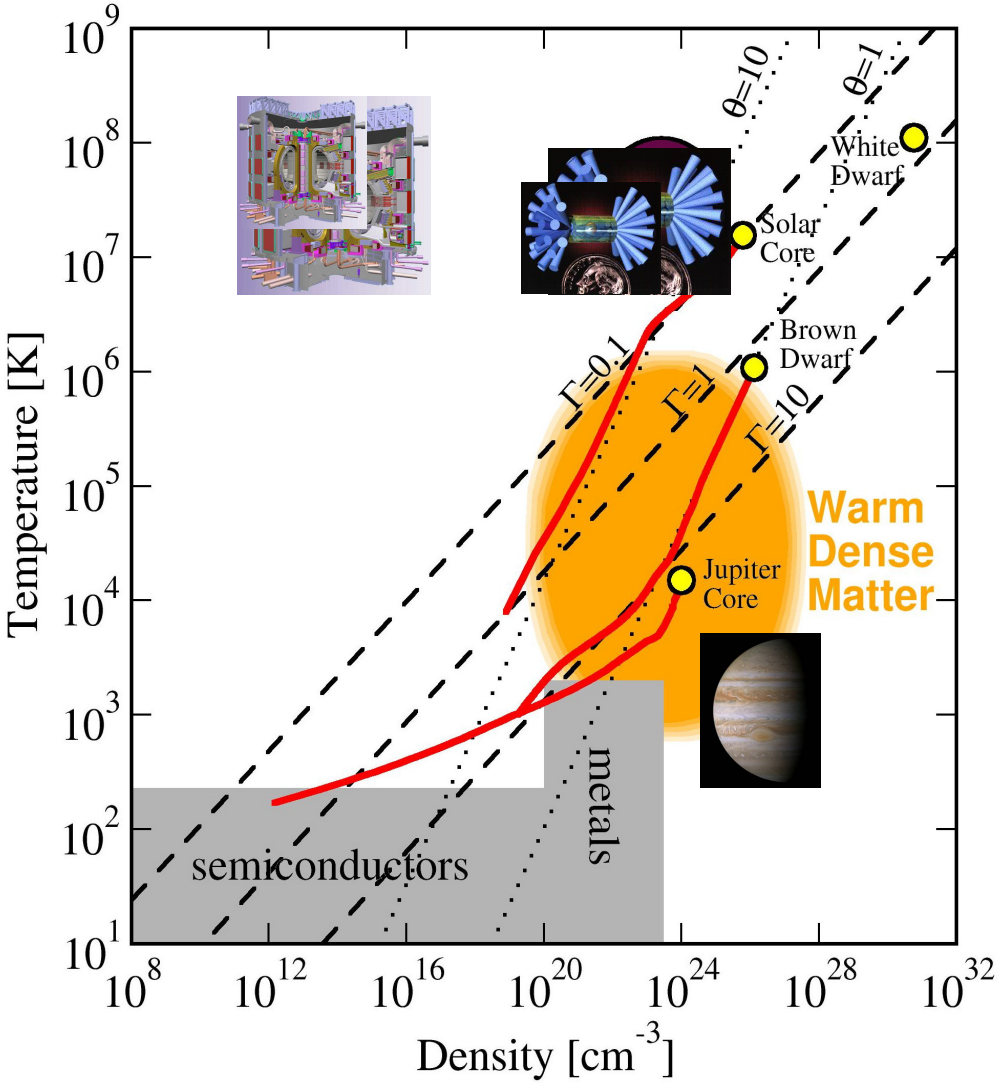
B. Militzer Phys. Rev. Lett 97, 175501 (October 2006).

Density-temperature plane
strong correlations and quantum effects in WDM

Plasma parameters:

coupling
$\Gamma=\ell/d$

degeneracy
$\Theta=k_B T/E_F$



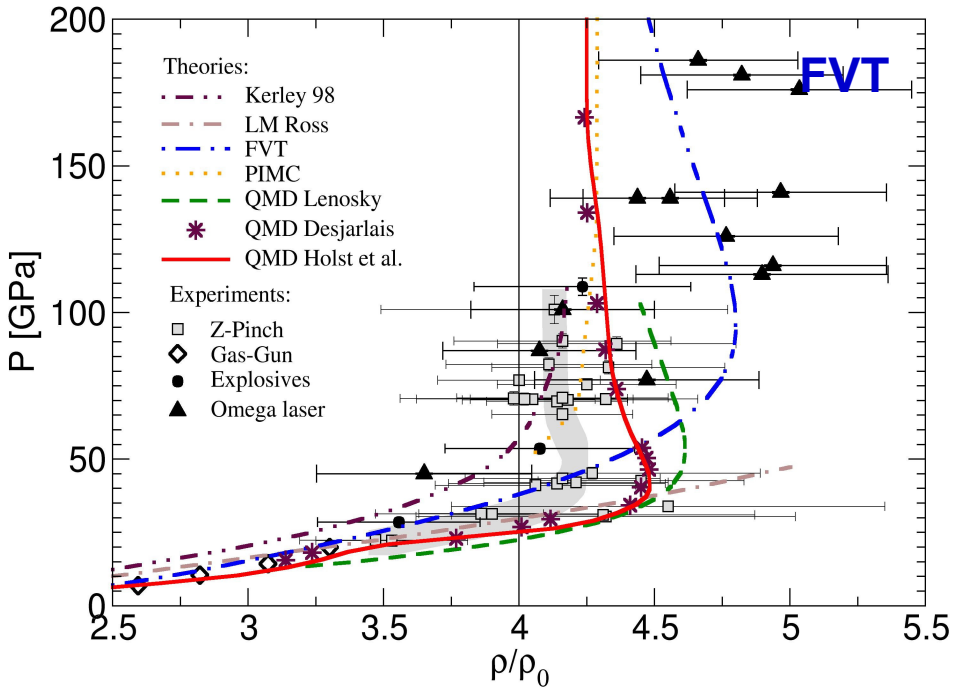
Shock waves probe WDM up to several Mbar (gas gun, Z pinch, explosions, laser).

States deep in interiors of GPs and BDs are not yet accessible.

Alternative:
X-ray pump-probe experiments, Thomson scattering
S.H. Glenzer, R. Redmer, Rev. Mod. Phys. (in print)

Hugoniot curve of warm dense D2

B. Holst, R. Redmer, M.P. Desjarlais, PRB 77, 184201 (2008)



PIMC correct high-T limit: B. Militzer and D. Ceperley, PRL 85, 1890 (2000).
Fully converged QMD: M.P. Desjarlais, PRB 68, 064204 (2003).
Z Pinch data: M.D. Knudson et al., PRB 69, 144209 (2004).
New Omega data: D.G. Hicks et al., PRB 79, 014112 (2009).
FVT chemical model: H. Juranek and R. Redmer, JCP 112, 3780 (2000).