

SMALL IS DIFFERENT
Emergent Phenomena at the
Nanoscale
(the non-scaleable regime)

Computers as Tools of Discovery
Proc. Nat. Acad. Sci. 102, 6671 (2005)

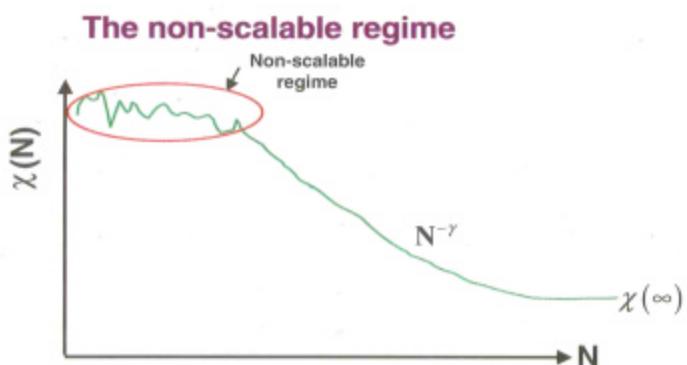
SMALL IS DIFFERENT
Computational Microscopies
of
Emergent Nanoscale Physical &
Chemical Phenomena
(the non-scaleable regime)

Computers as Tools of Discovery
Proc. Nat. Acad. Sci. 102, 6671 (2005)

THE INTERSECTION OF TWO MAJOR EMERGENT MOVEMENTS

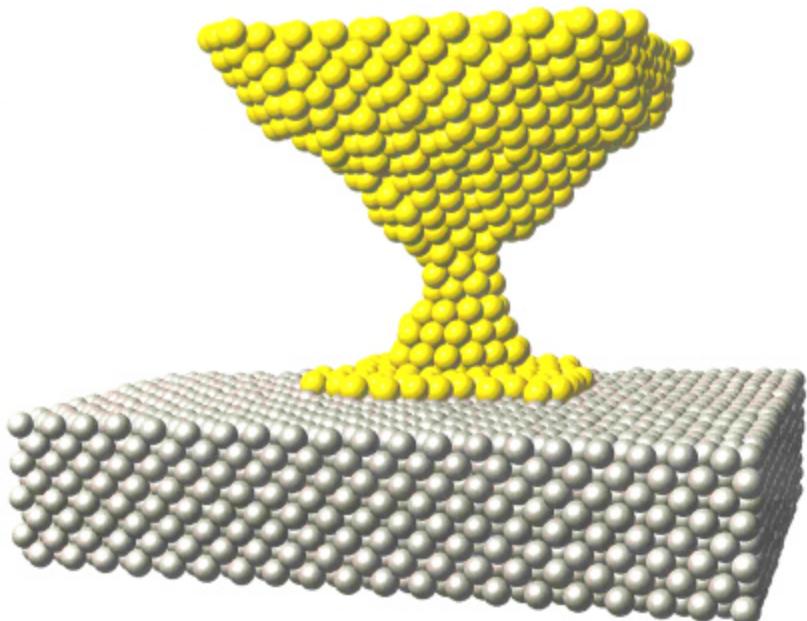
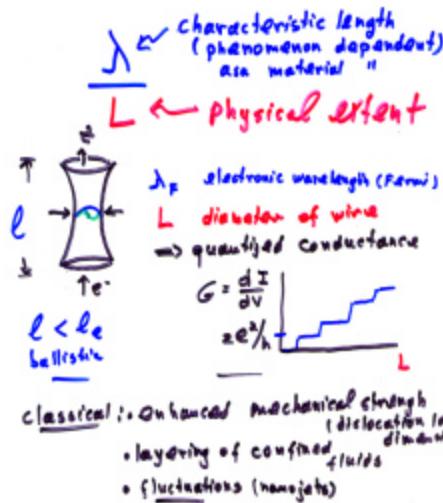
- * SCIENCE AND TECHNOLOGY AT THE NANOSCALE – **SMALL IS DIFFERENT**
- * COMPUTATIONAL MICROSCOPIES – **COMPUTERS AS TOOLS FOR DISCOVERY**

Small is Different

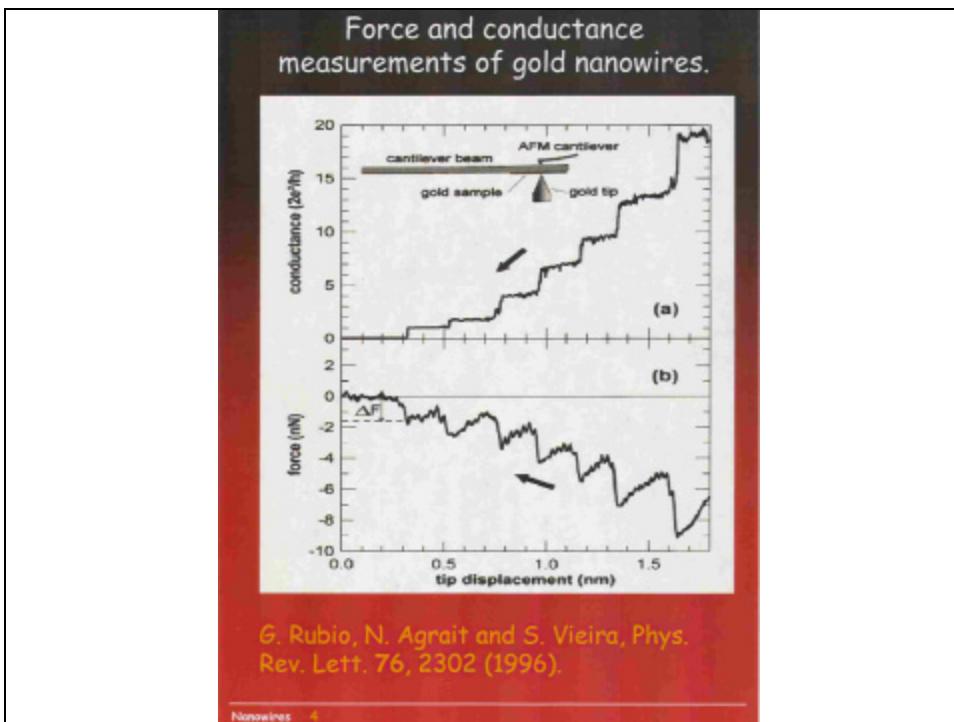
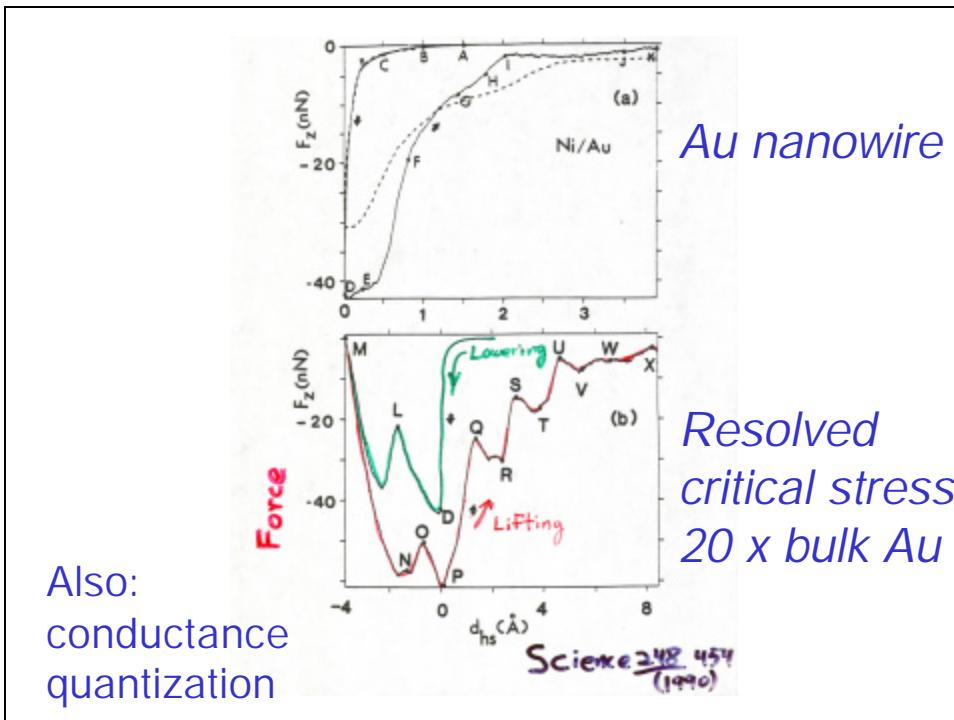


SMALL IS DIFFERENT

Nano
 (Nanos, Greek) dwarf)
 $1\text{nm} = 10^{-9}$ meter
 $1\text{nm} = 10^{-7}$ centimeter
 $1\text{nm} = 10$ Angströms



Quedde + Landman JVST (1991); Science 248, 454 (1990)



NON-SCALEABILITY

EACH

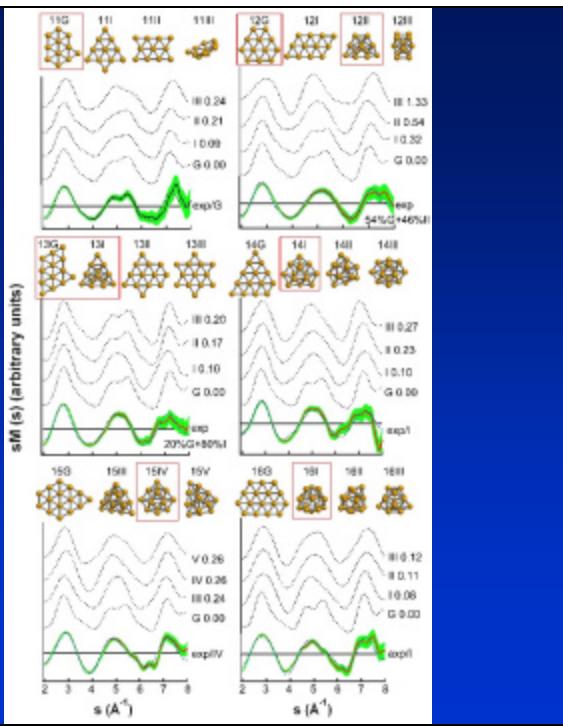
ATOM

COUNTS

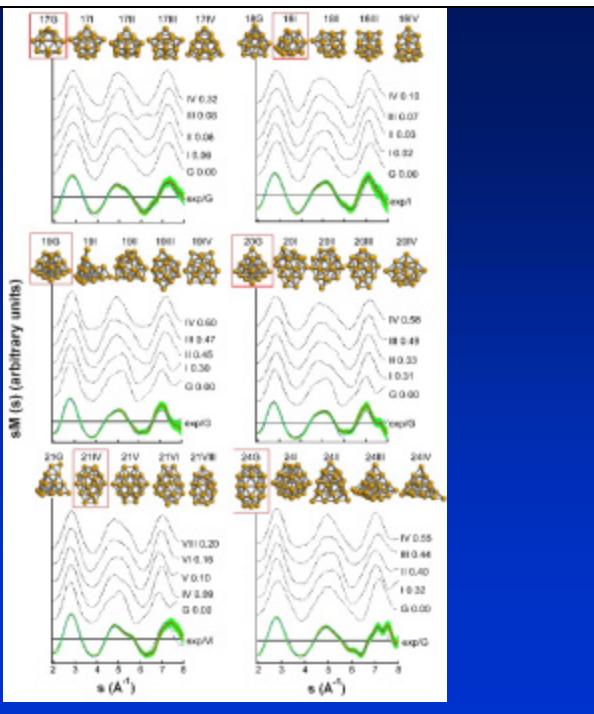
Golden Stories

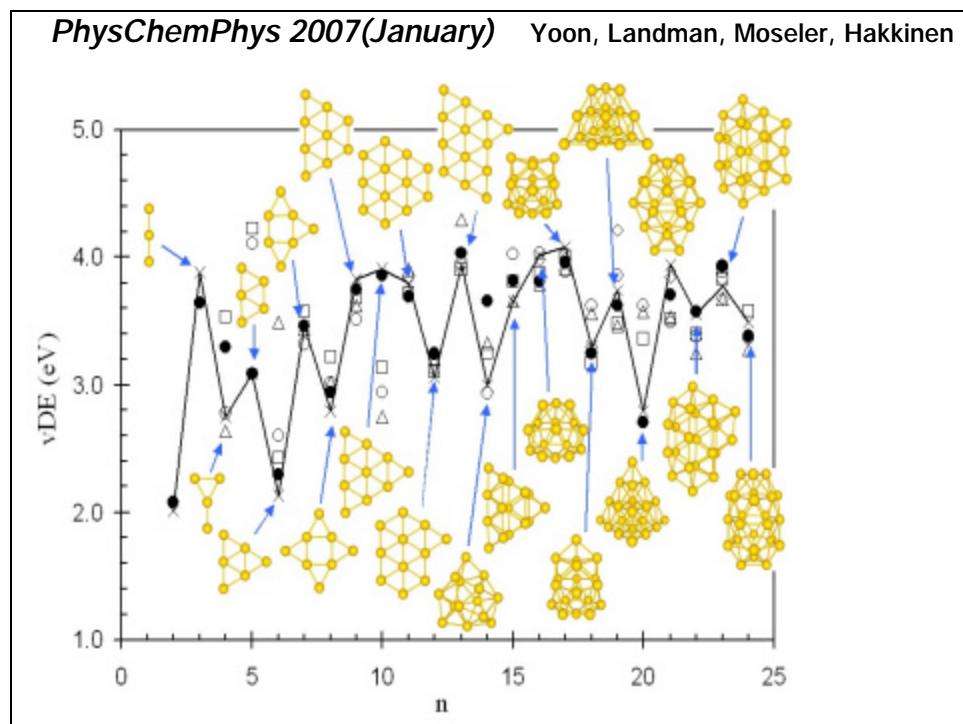
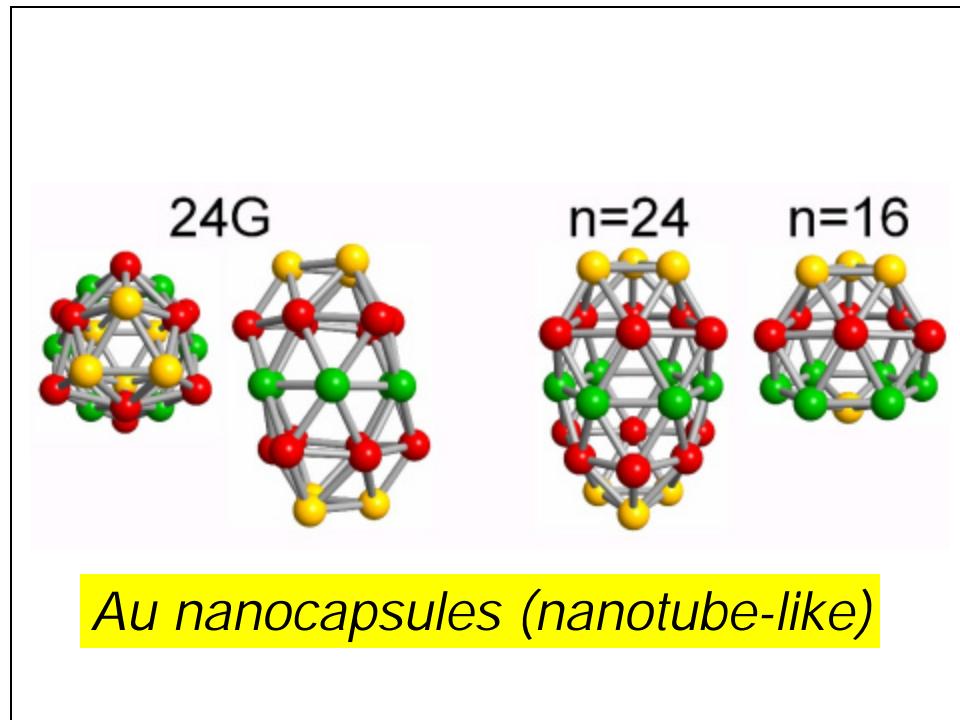
*Xing, Parks
Yoon, Landman
Phys. Rev. B
Nov 15 ('06)*

*Electron diffraction +
First principles (DFT)
Structural search &
optimization*

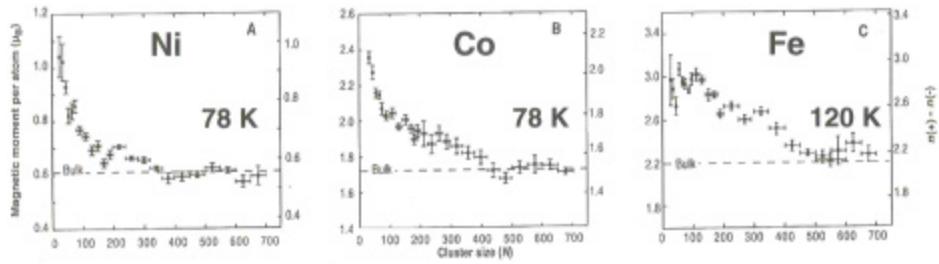


*Xing, Parks,
Yoon,
Landman
PRB Nov 15
('06)*





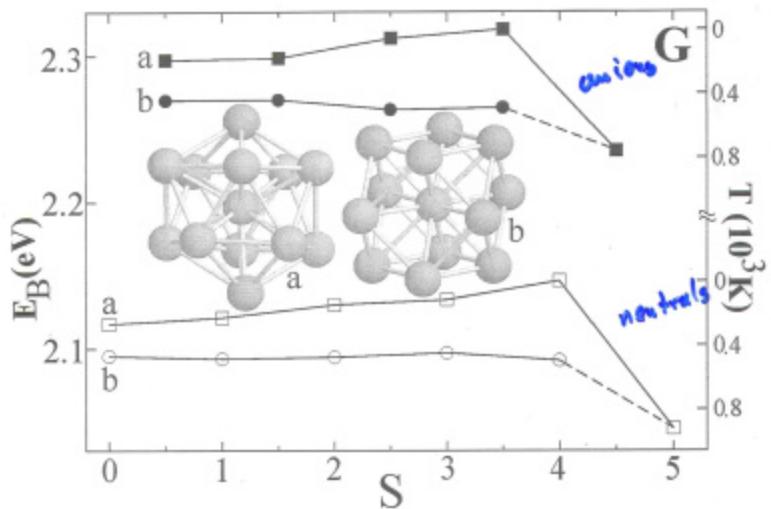
Low-temperature Average Magnetic Moment per Atom in Metal Clusters

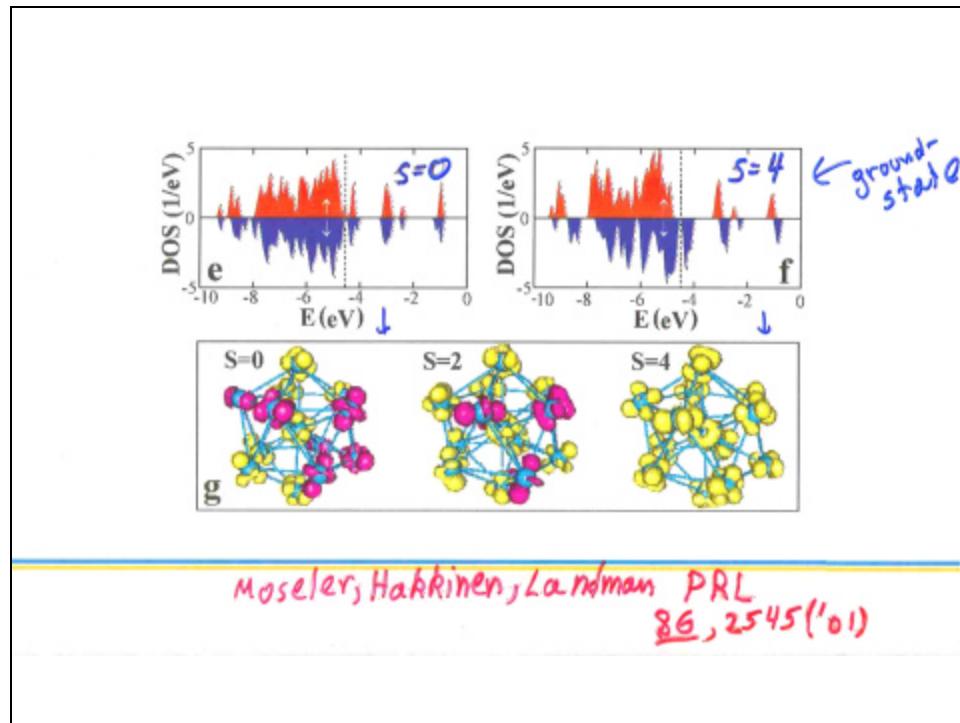
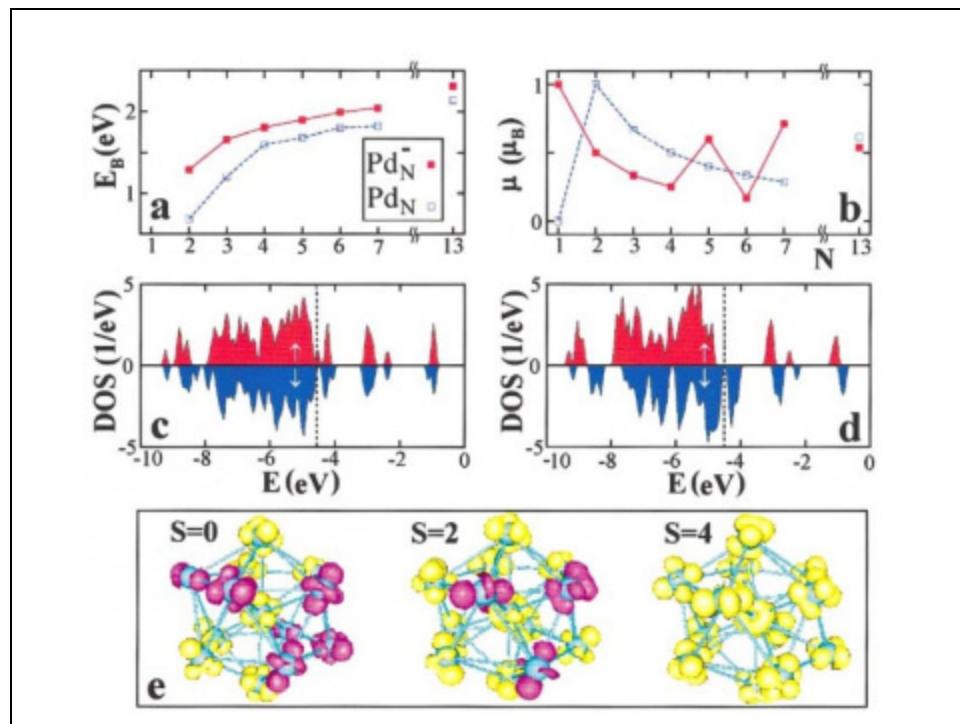


I.M. L. Billas, A. Chatelain, and W. A. de Heer, Science 265, 1682 (1994)

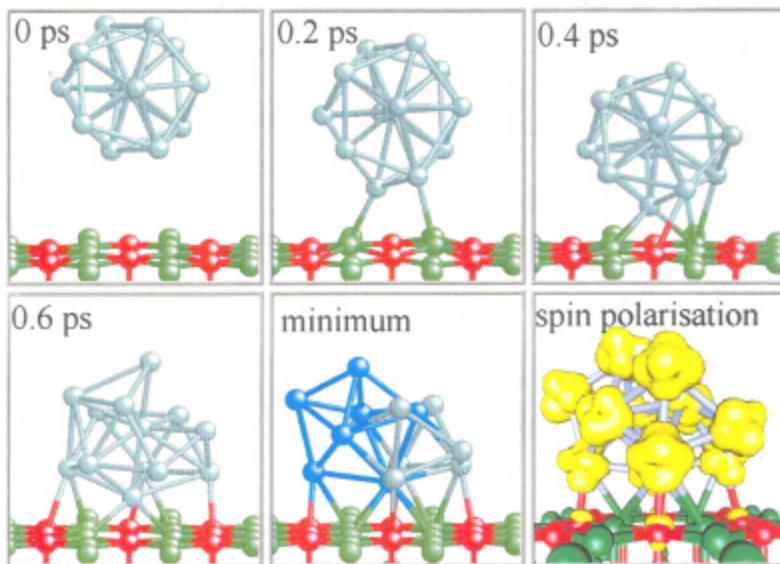
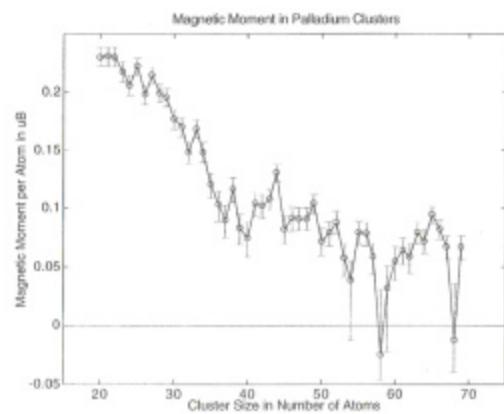
Nanocluster magnets

Pd₁₃





Most Recent Experiments (unpublished) School of Physics, GA Tech



Nano-Scale Matter

- **Nature: Novel Phenomena**
 - reduced length and time scales
 - emergent phenomena
 - not merely scaling down!!
- **Experiment and Theory: New Strategies and Methodologies**
 - ultra-high spatio-temporal resolution
 - atomic-scale manipulations
 - simulations (quantum *ab-initio* and classical)
- **Science-driven Novel Technologies**
 - New design concepts; new opportunities

Complexity & Size

EMERGENCE

Emergent Phenomena

Phenomena which are not the properties of the individual elementary components
BUT of the assembly of such components

- ⇒ Often accompanied by
(Spontaneous Symmetry Breaking)
Phenomena which are not evident (and are not part of) the formulation of the problem

Example:

$$H = \sum_i H(i) + \sum_{i,j} V(i,j) + \sum_{i,j,k} V(i,j,k)$$

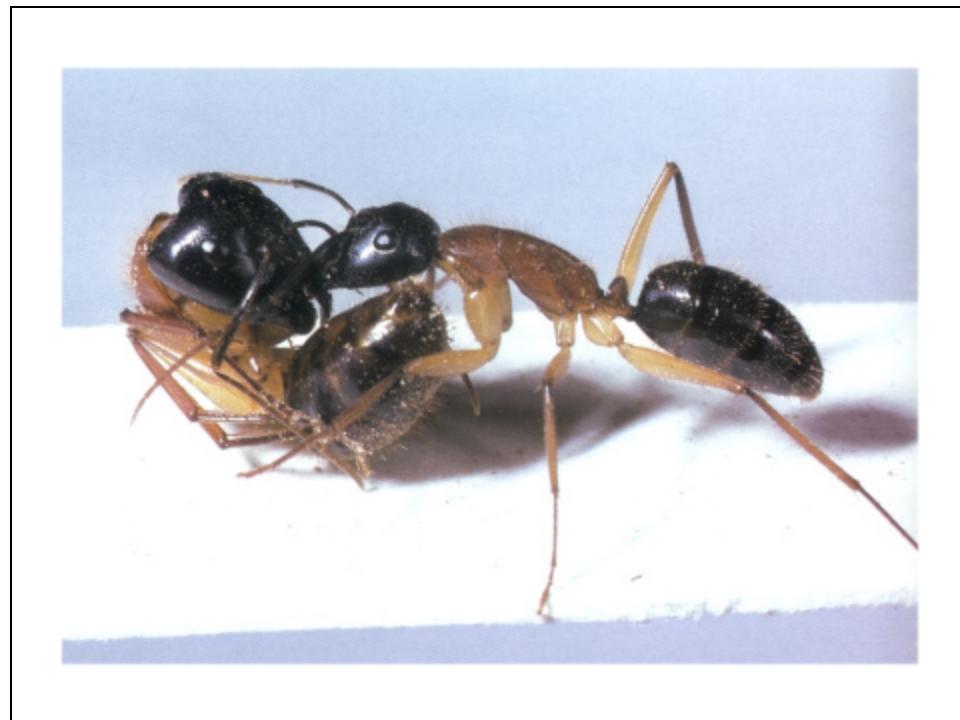
Emergent Phenomena

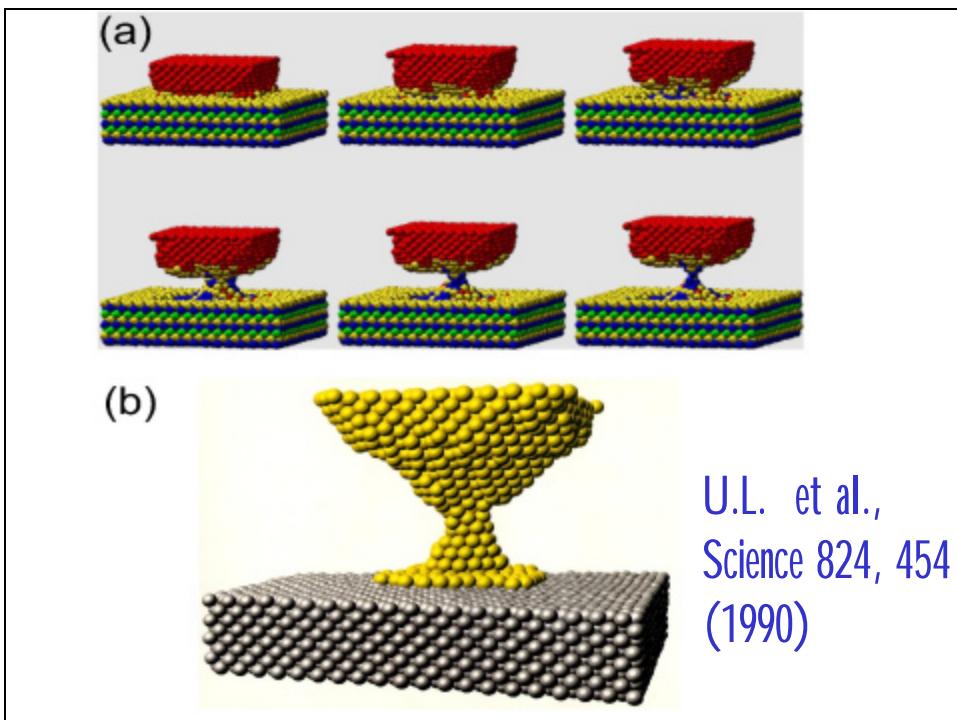
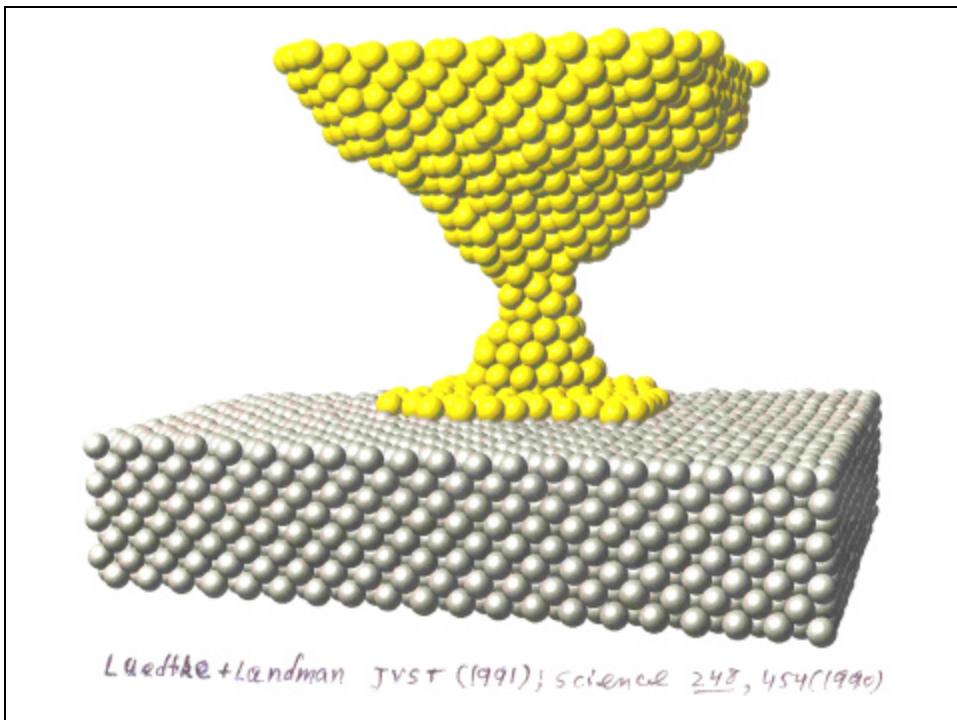
The movement from **low-level** rules to **higher-level** sophistication

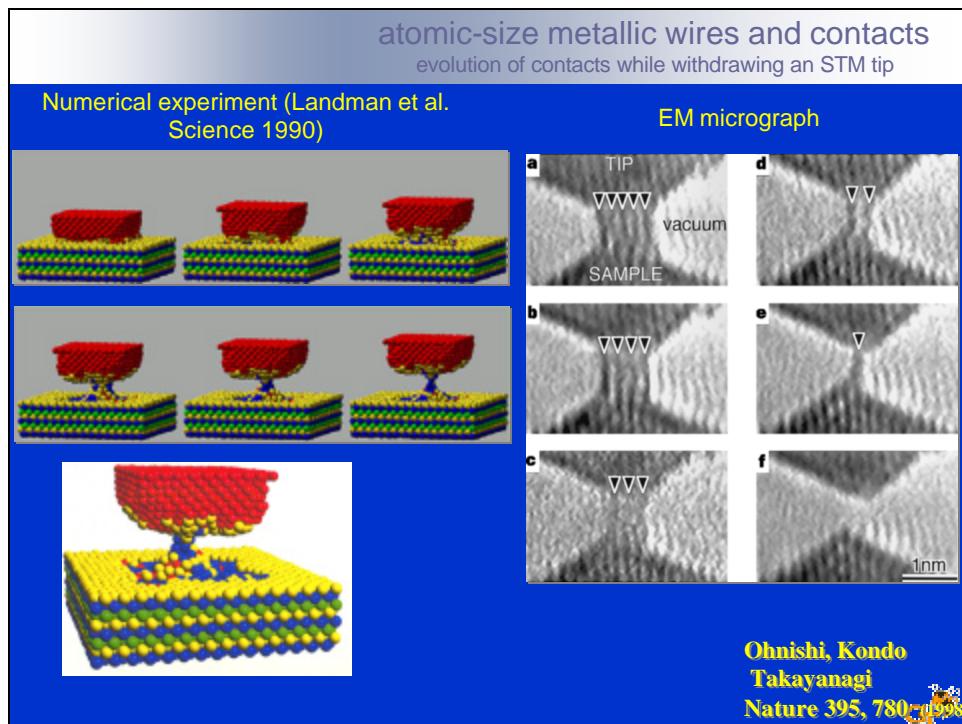
When agents residing on **one scale** start producing behavior that lies on a **higher scale**

Higher-level, large-scale, pattern arising out of **local interactions** between individual components

Ants → Colonies ; Urbanites → Cities
Atoms → Crystals ; Electrons → Wigner Crystallites







SELF ASSEMBLY
SELF ORGANIZATION
***SELF SELECTION OF
SIZE, SHAPE & FORM***

NATURE'S WAY

COMPUTATIONS AS TOOLS IN EXPLORATION OF EMERGENT PHENOMENA

Enable the discovery of emergent complex behavior or patterns, with minimal coarse graining and/or simplifying model assumptions ("brute force")

Nano-Scale Matter

- **Nature: Novel Phenomena**
 - reduced length and time scales
 - emergent phenomena
 - not merely scaling down!!
- **Experiment and Theory: New Strategies and Methodologies**
 - ultra-high spatio-temporal resolution
 - atomic-scale manipulations
 - simulations (quantum *ab-initio* and classical)
- **Science-driven Novel Technologies**
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Complexity & Size

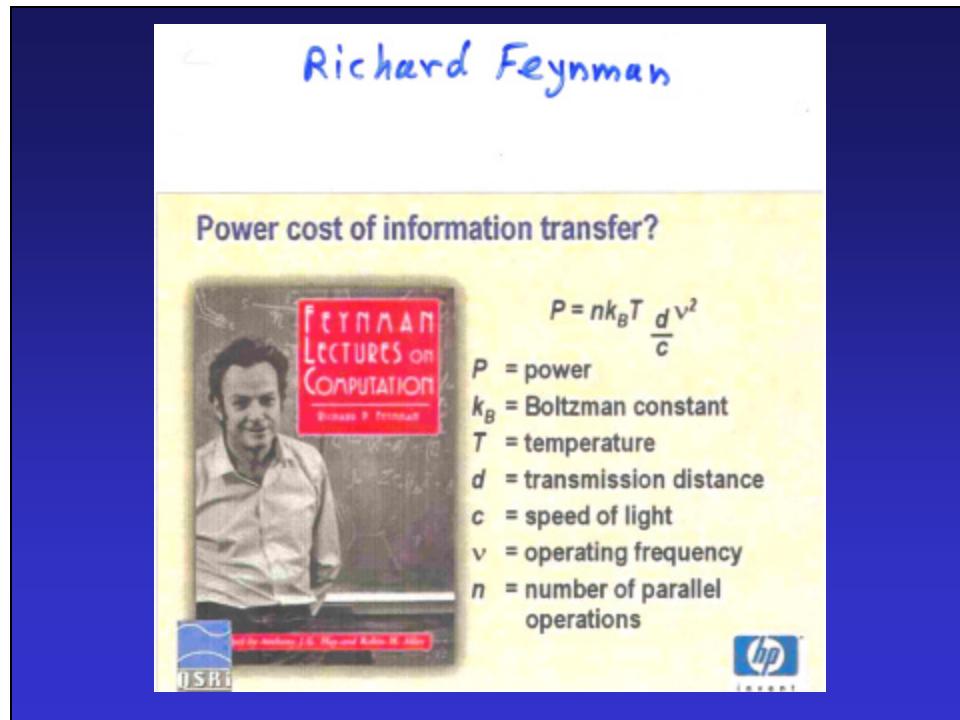
*The Science of
Today Is the
Technology of
Tomorrow*



Nano-Scale Matter

Principles

- **Self-assembly** (“irrational” synthesis)
- **Self-selection**
abundance, size (magic numbers), **shape!!**
- **Fluctuations**
- **Spontaneous Symmetry Breaking**



NATURE VOL. 334 18 AUGUST 1988

NEWS AND VIEWS

561

Statistical mechanics by numbers

Molecular dynamics is proving a useful technique well away from the applications for which it was originally devised. A guiding principle is to make a virtue of simplicity.

MOLECULAR dynamics is clearly well on the way to being a universal tool, as if it were the differential calculus. So much is plain from the range of problems now being tackled, and sometimes at least partially solved, by the application of this technique. Gone, it seems, are the days when people's ambitions in the field were restricted to the calculation of the properties of smallish molecules, with only distant hopes of being able to tackle the problems of, say, protein molecules. Now, molecular dynamics is being used to tackle problems which are quite general.

A recent issue of *Physical Review Letters* (25 July), for example, contains accounts of applications of the technique to the solution of the Navier-Stokes equation on the one hand and the surface melting of aluminium crystals on the other. The statement that all this has been made possible by the arrival of computer power in very substantial amounts is easy, almost banal, but it is only half the truth. The kinds of tasks now being taken up demand an undivided degree of ingenuity

—dreds of particles should be calculable is not as great an impediment as that of arranging that the method of calculation is not a recipe for accumulating and then multiplying error from one step to the next. But there is evidently no reason why the same techniques should not in principle at least be applied to systems other than simple molecular systems. Indeed, in some respects, three-dimensional systems such as liquids may be more tractable than molecules, if only because the need to specify the force-law governing the interaction between each pair of particles may be enormously simplified for a homogeneous system, for example, there is at most one force-law to worry about.

The problem of melting is a good place at which to start. P. Stolze and J. K. Norsoy from the Technical University of Denmark at Lyngby and U. Landman from the Georgia Institute of Technology (*Phys. Rev. Lett.* 61 440; 1988) begin by remarking on the conflict of evidence and inference on the question of whether the melting of a solid begins as a surface phenomenon

The calculation of the dynamical properties of liquids (by M. E. Colvin, A. J. C. Ladd and B. J. Alder of the Lawrence Livermore National Laboratory, *Phys. Rev. Lett.* 61 381; 1988) may be even more portentous. What this group had done is to simulate the flow of a fluid by "stripping standard hard-disk molecular dynamics to its bare essentials". In other words, the world in which elements of a fluid (not necessarily atoms) are dealt with as if they were billiard balls (or disks in two dimensions) colliding by Newton's laws is replaced by that in which directional homogeneity is done away with by means of the supposition that the elements of the fluid are rigid hexagons (in two dimensions), each with the same orientation.

One advantage of this representation of a fluid in motion is that it is relatively easy to enumerate the kinds of collisions allowed; in this model, ten classes of collisions suffice. Each collision turns a pair of particles, whose velocities are specified, into another pair of particles whose velocities follow from the enumerated collisions.

John Maddox

© 1988 Nature Publishing Group

The fundamental laws necessary for the mathematical treatment of a **large part of physics and the whole of chemistry** are thus completely known, and the difficulty lies only in the fact that application of these laws leads to **equations that are too complex to be solved.**

P.M. Dirac (1929)

Computational Microscopy

- Simulations of materials properties and processes
- Computational experiments
- **Interpret (analysis of observations)**
- **Unify (sets of observations)**
- **Predict**

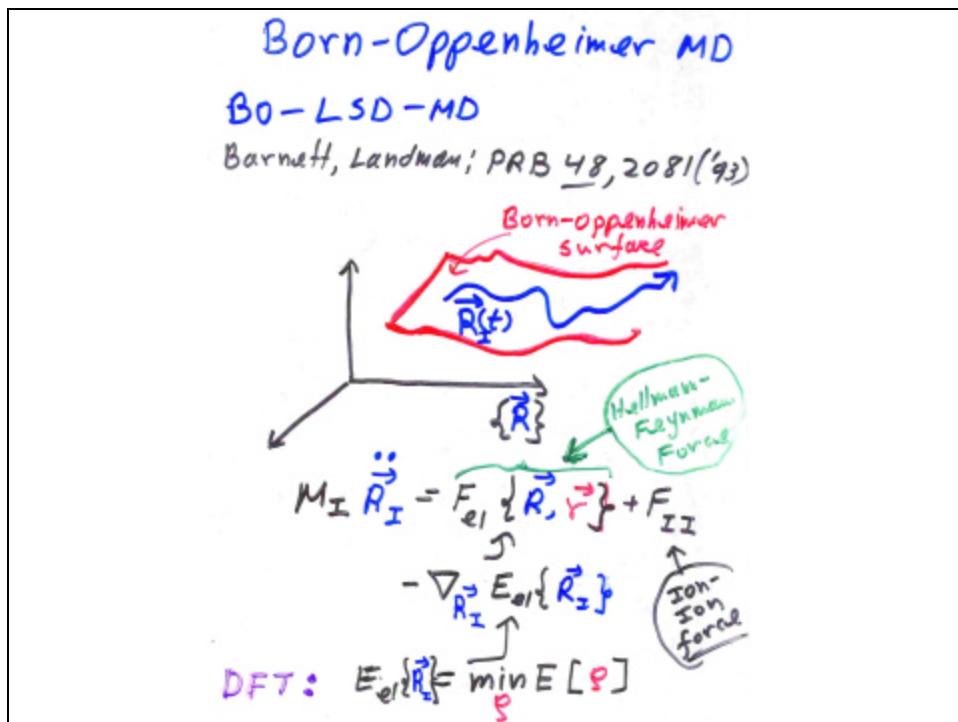
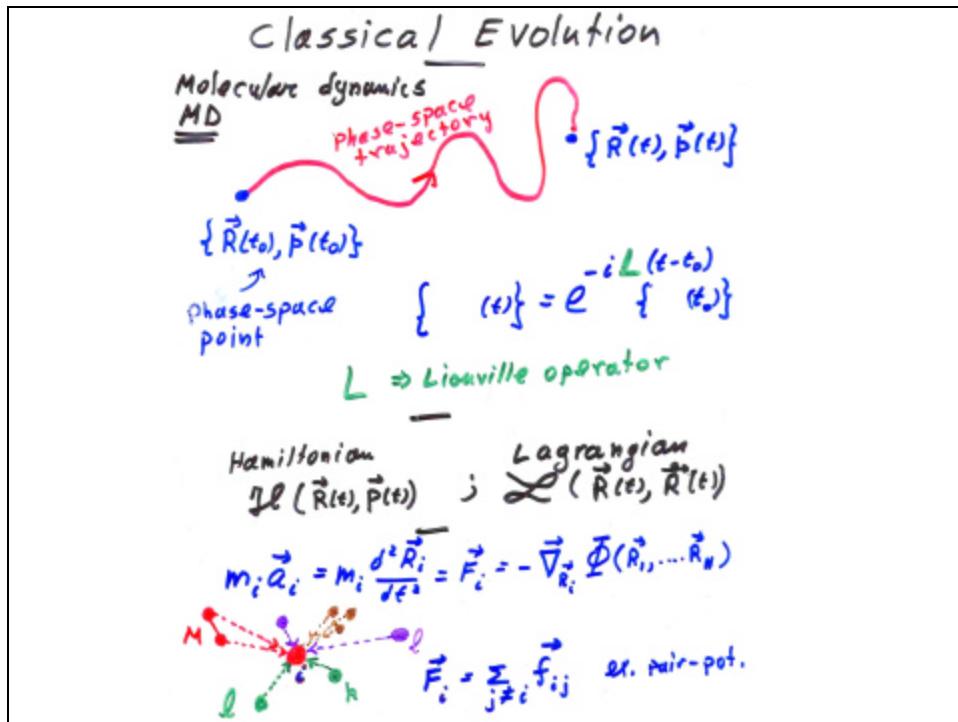
***The Scientist is not the person
who always gives the
right answers,
he is
one who asks the
right questions***

Claude Levi- Strauss (1908-)

Nano-Scale Matter

Principles

- **Self-assembly** (“irrational” synthesis)
- **Self-selection**
abundance, size (magic numbers), **shape!!**
- **Fluctuations**
- **Spontaneous Symmetry Breaking**



NON-SCALEABILITY

EACH

ATOM

COUNTS

NON-SCALEABILITY

EACH

ATOM

COSTS

QM/MM scheme

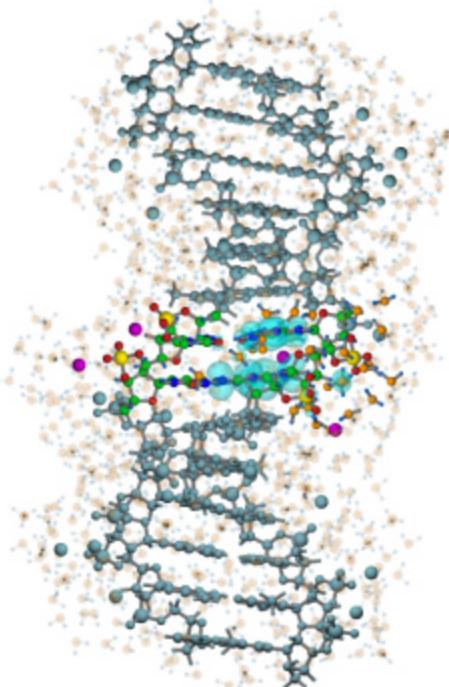
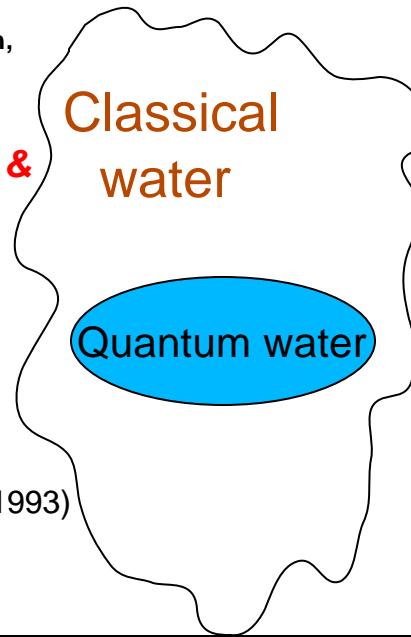
A.Bongiorno, R.N. Barnett, Y. Li, S.B. Suh,
D. Ricci, C.L. Cleveland, U. Landman

**COMBINING QUANTUM (QM) &
CLASSICAL TREATMENTS**

QUANTUM: SDFT/GGA (PBE)
Self-interaction correction (SIC)
Soft pseudopotentials
Plane-wave basis (62 Ry)

Barnett & Landman, PRB **48**, 2081 (1993)

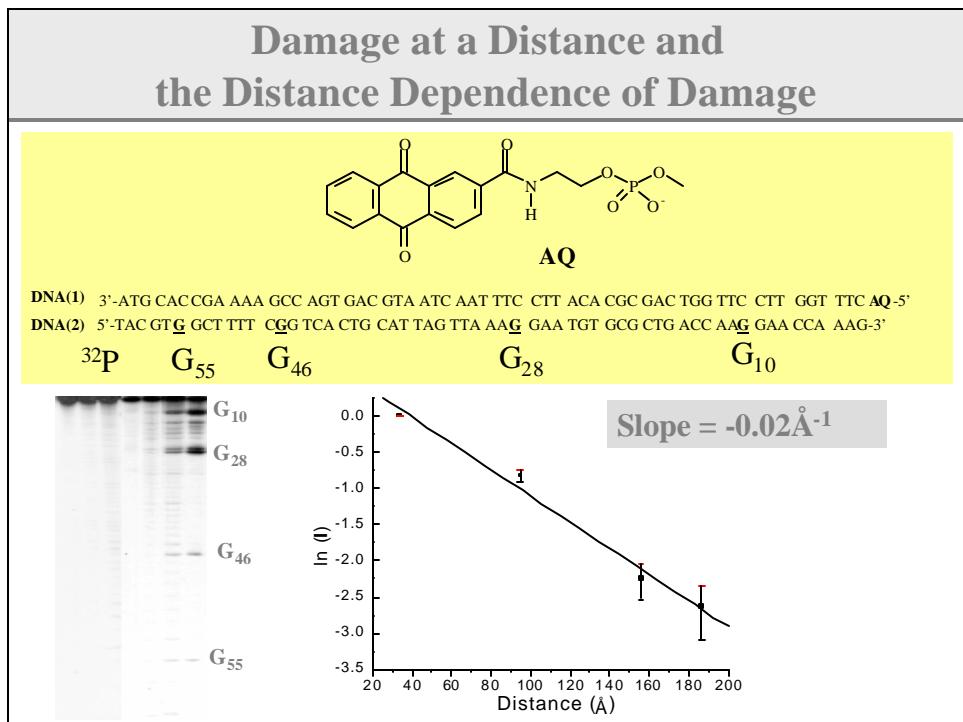
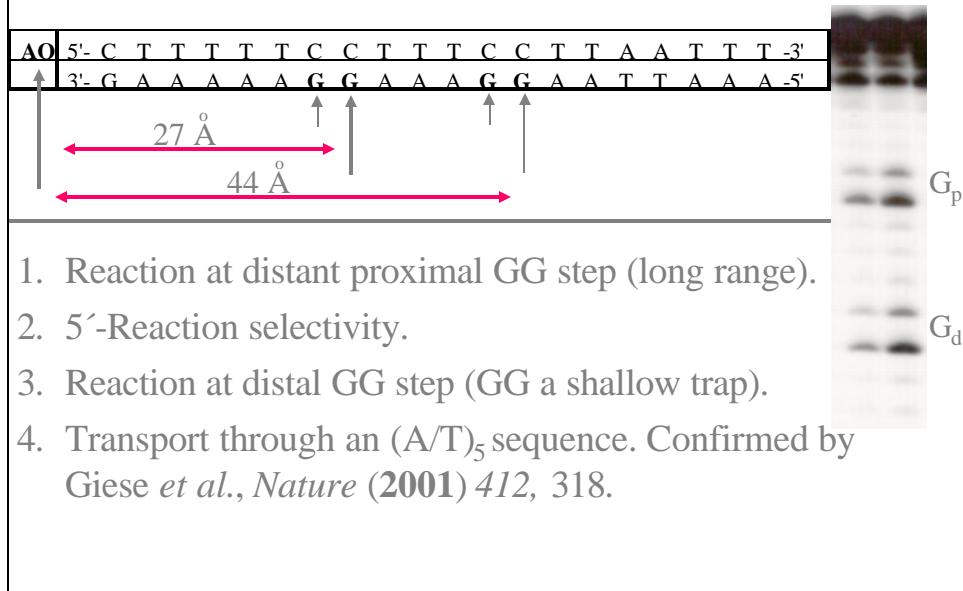
CLASSICAL: TIP3P (Jorgensen)



**Transport &
Reaction,
Mutagenesis,
DNA damage
& repair**

*Barnett, Cleveland,
Bongiorno, Landman
Abraham, Schuster*
Science 294, 567 ('01)
JACS 128, 10798 ('06)
JACS ('07)

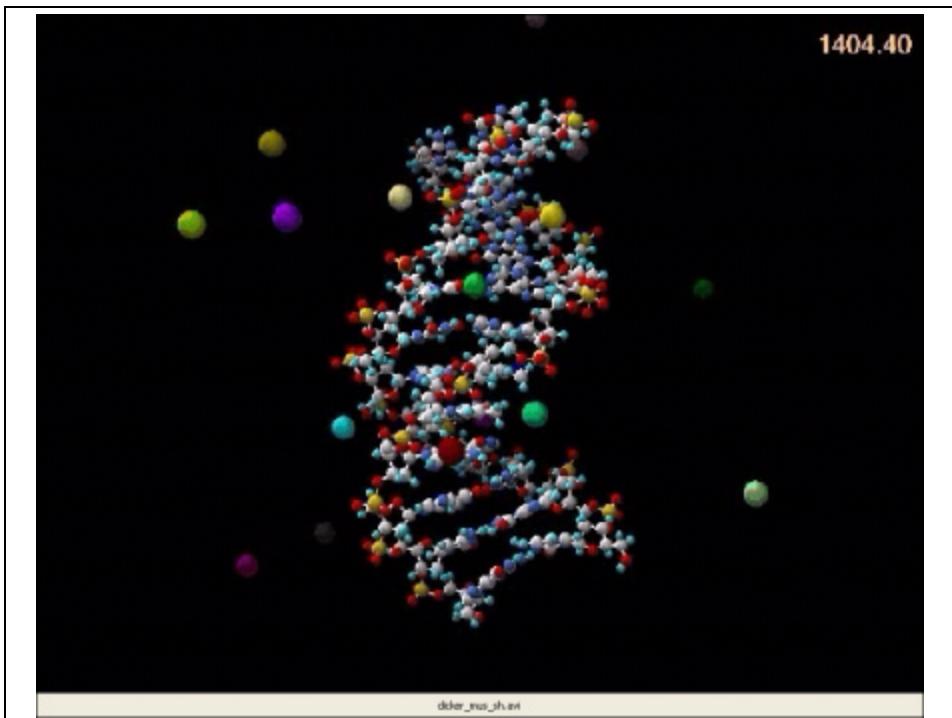
Anthraquinone Covalently Linked to a 5'-Terminus of DNA
 Gasper and Schuster, *J. Am. Chem. Soc.* (1997) 119, 12762

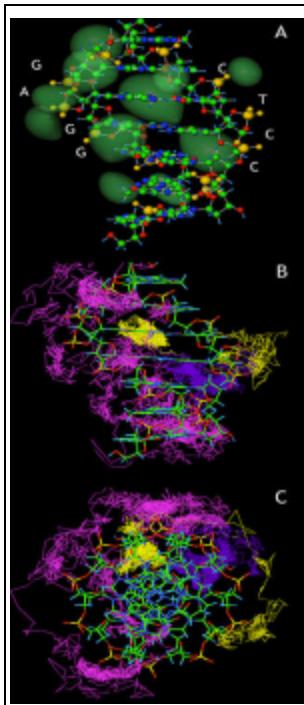


Electron Transfer Reactions: Acceptor-Bridge-Donor (ABD) Systems.

Transport Models

1. Coherent single-step tunneling processes with charge localized on initial and final states (**Acceptor and Donor**). DNA acts as a molecular wire.
2. Incoherent random-walk multi-step hopping between initial and final states, where hops between sequential guanines (**hole resting sites**) are mediated by superexchange across intervening A/T sequences (**bridges**).
3. Polaron-like hopping process where local energy-lowering dynamical structural distortion gives a self-trapped state with a finite spatial extent. Thermal hopping transports the polaron from one location to another.





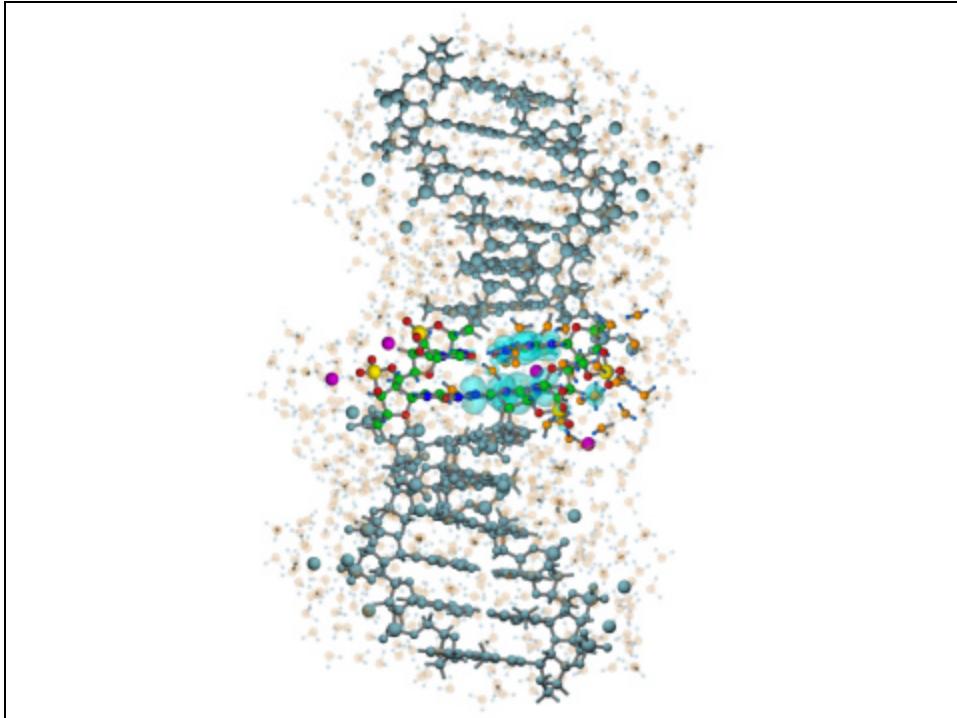
ION-GATED CHARGE TRANSPORT

Classical Molecular Dynamics Simulation of Duplex

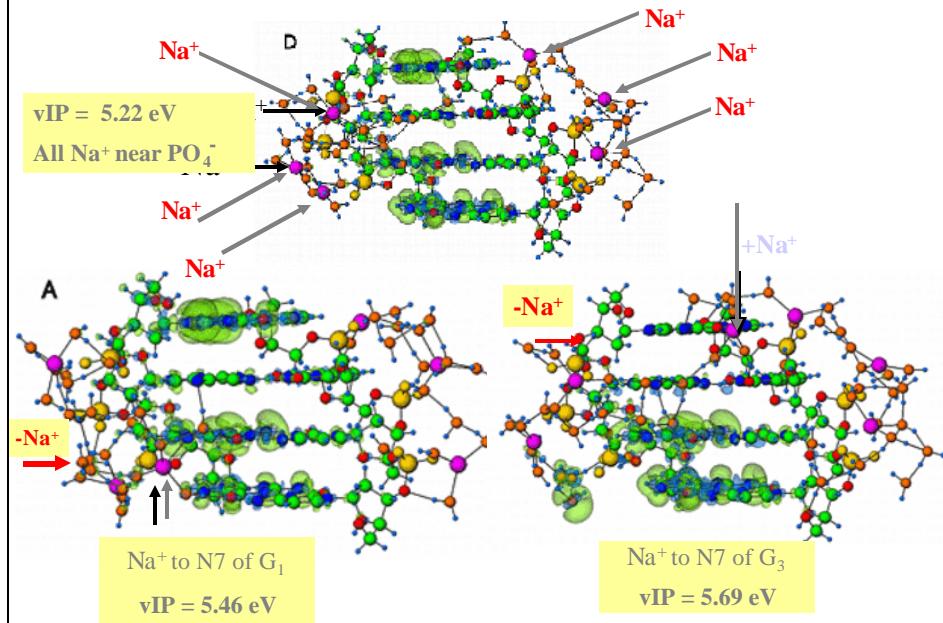


- Solvating water molecules not shown
- Trajectories are 1.4 nanoseconds

Na⁺ (1) —————
Na⁺ (2) —————
Na⁺ (3) —————

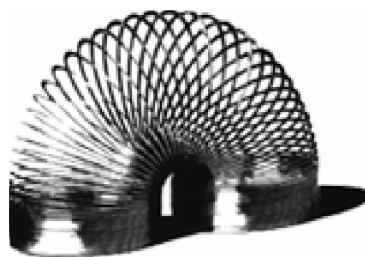


COUNTER-ION GATED HOLE TRANSPORT



Phonon-Assisted Polaron-Like Hopping.

A Mechanism for Charge Transport in Duplex DNA.



Slinky - Compression (distortion) moves through the spring when coils are added or lost from the compression

Oxidative damage to DNA

Counter ion-assisted reaction with water

**Robert N. Barnett, Angelo Bongiorno,
Charles L. Cleveland, Abraham Joy,
Uzi Landman, Gary B. Schuster**

JACS, 128, 10798 (2006)

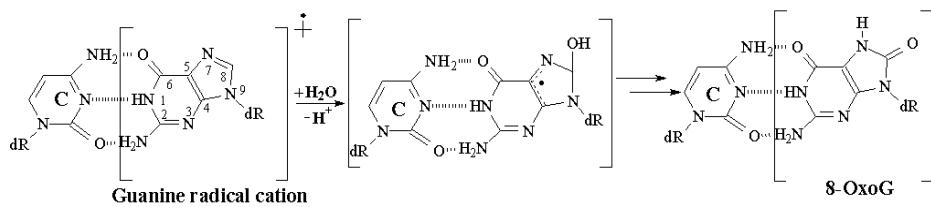
Oxidative damage to DNA

Sequence dependence of the reaction with water

**Angelo Bongiorno, Robert N. Barnett,
Charles L. Cleveland, Abraham Joy,
Uzi Landman, Gary B. Schuster**

(JACS, 2007)

schematic water reaction with DNA radical cation



Error-prone replication of oxidatively damaged DNA by a high-fidelity DNA polymerase

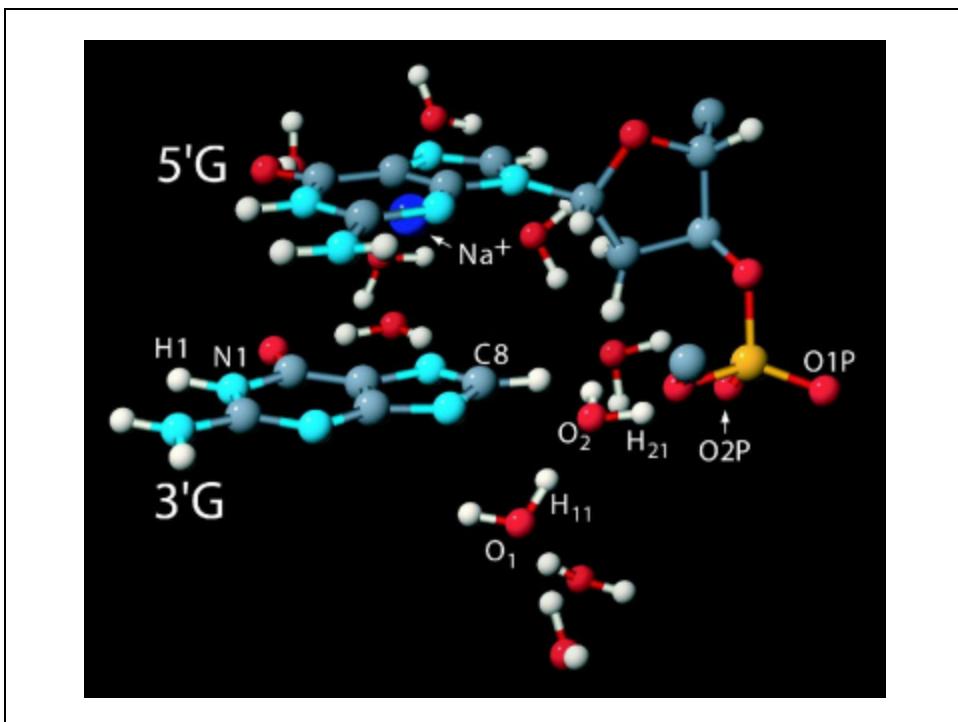
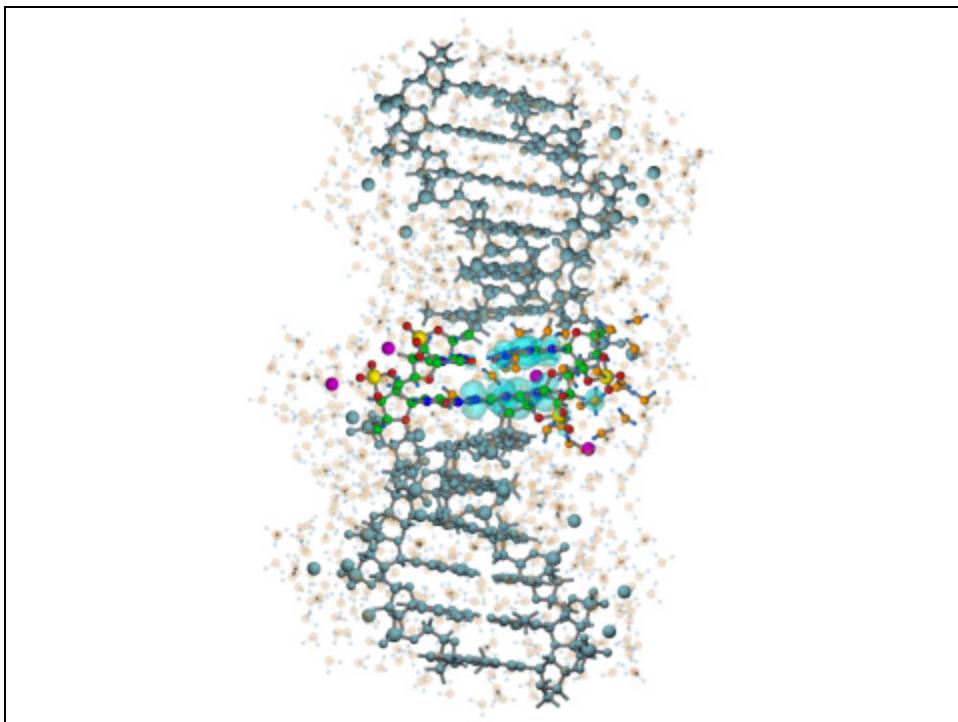
Gerald W. Hsu¹, Matthias Ober², Thomas Carell² & Lorena S. Beese¹

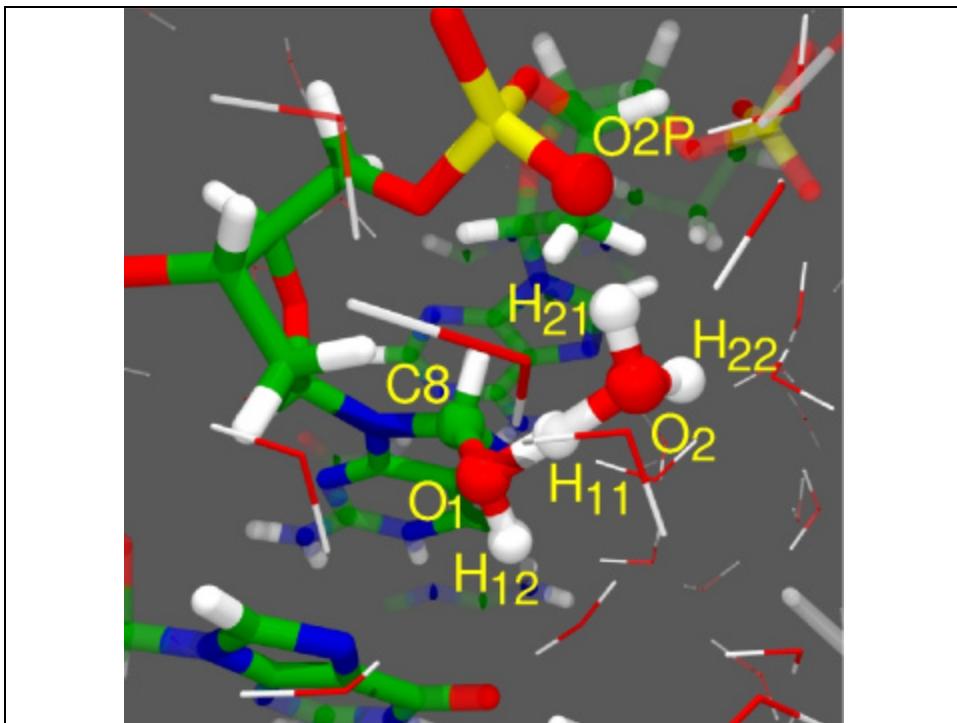
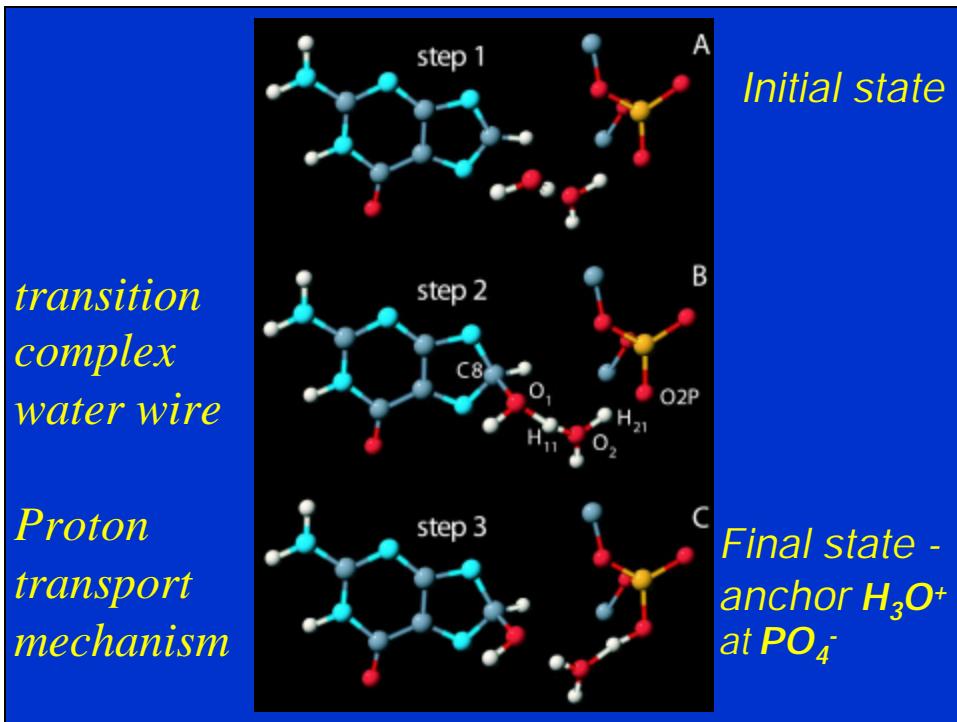
¹Department of Biochemistry, Duke University Medical Center, Durham, North Carolina 27710, USA

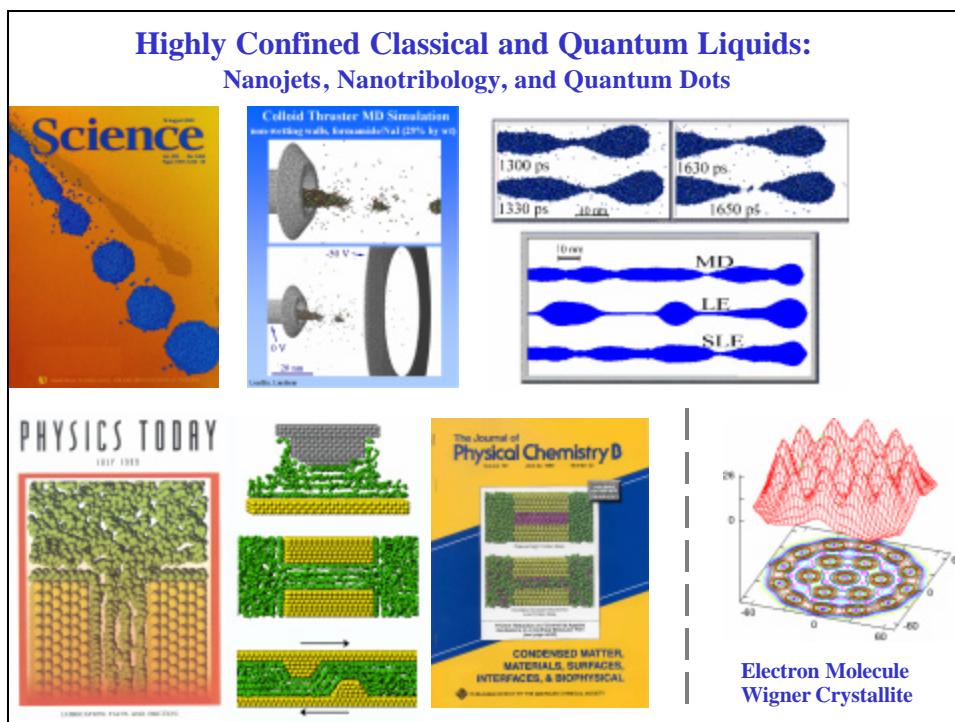
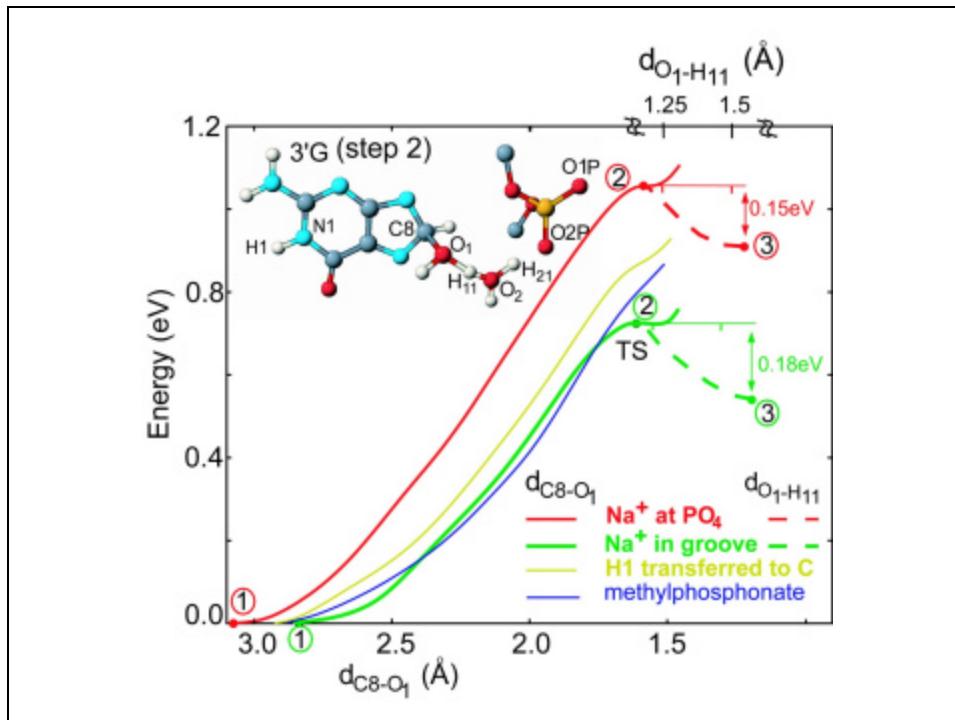
²Department of Chemistry and Biochemistry, Ludwig-Maximilians-Universität München, Butenandtstraße 5–13, D-81377 Munich, Germany

Aerobic respiration generates reactive oxygen species that can damage guanine residues and lead to the production of 8-oxoguanine (8oxoG), the major mutagenic oxidative lesion in the genome¹. Oxidative damage is implicated in ageing² and cancer, and its prevalence presents a constant challenge to DNA polymerases that ensure accurate transmission of genomic information. When these polymerases encounter 8oxoG, they frequently catalyse misincorporation of adenine in preference to accurate incorporation of cytosine³. This results in the propagation of G to T transversions, which are commonly observed somatic mutations associated with human cancers^{4,5}. Here, we present sequential snapshots of a high-fidelity DNA polymerase during both accurate and mutagenic replication of 8oxoG. Comparison of these crystal structures reveals that 8oxoG induces an inversion of the mismatch recognition mechanisms that normally proofread DNA, such that the 8oxoG:adenine mismatch mimics a cognate base pair whereas the 8oxoG:cytosine base pair behaves as a mismatch. These studies reveal a fundamental mechanism of error-prone replication and show how 8oxoG, and DNA lesions in general, can form mismatches that evade polymerase error-detection mechanisms, potentially leading to the stable incorporation of lethal mutations.

**Nature
(2005)**



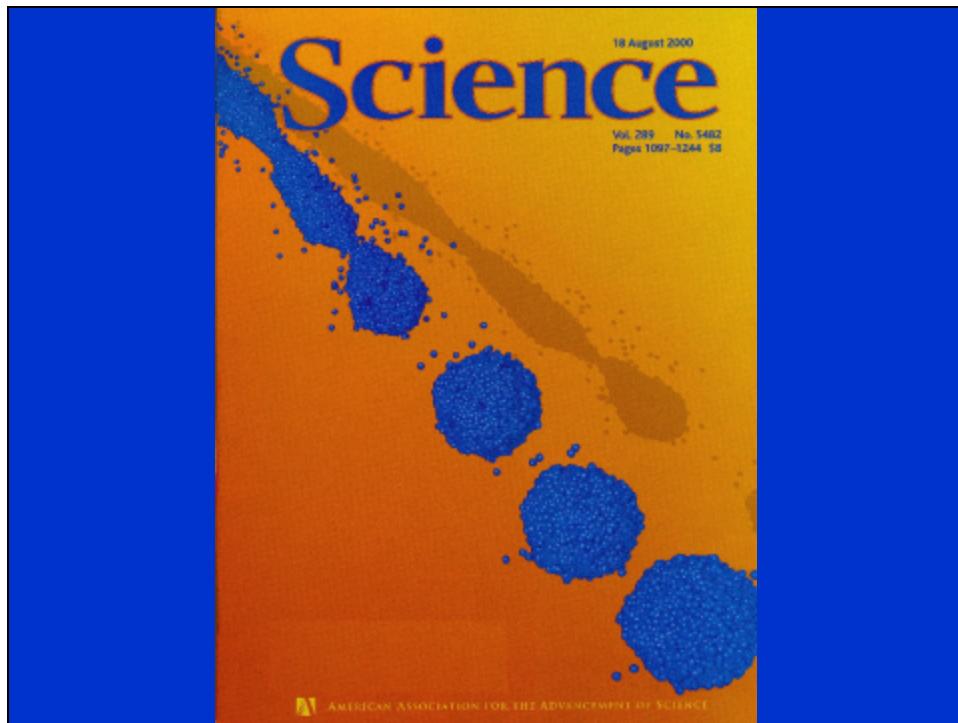


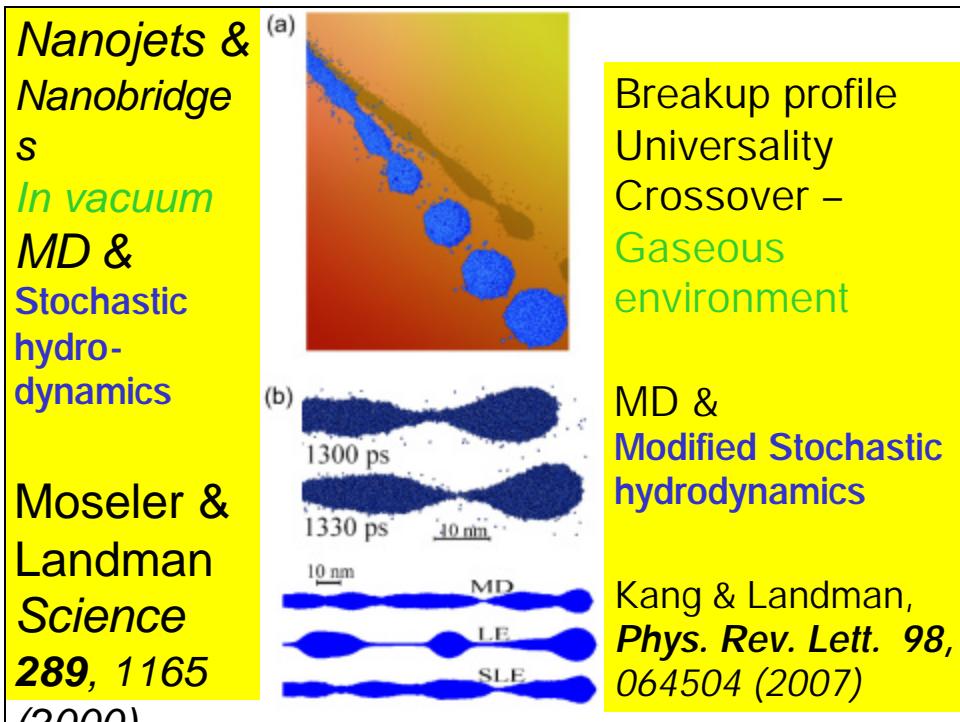


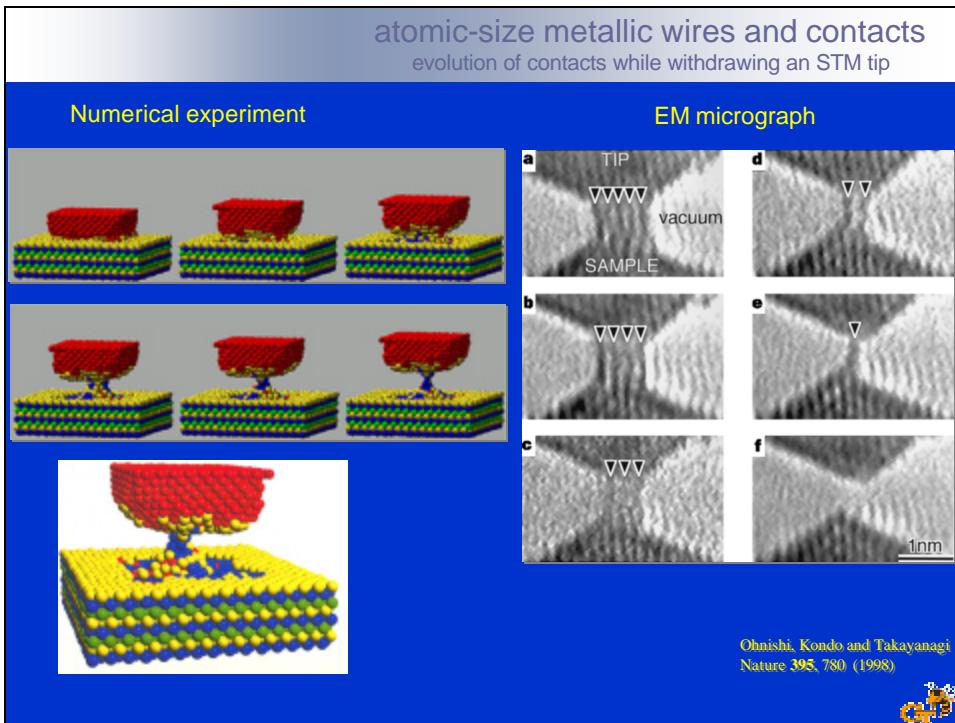
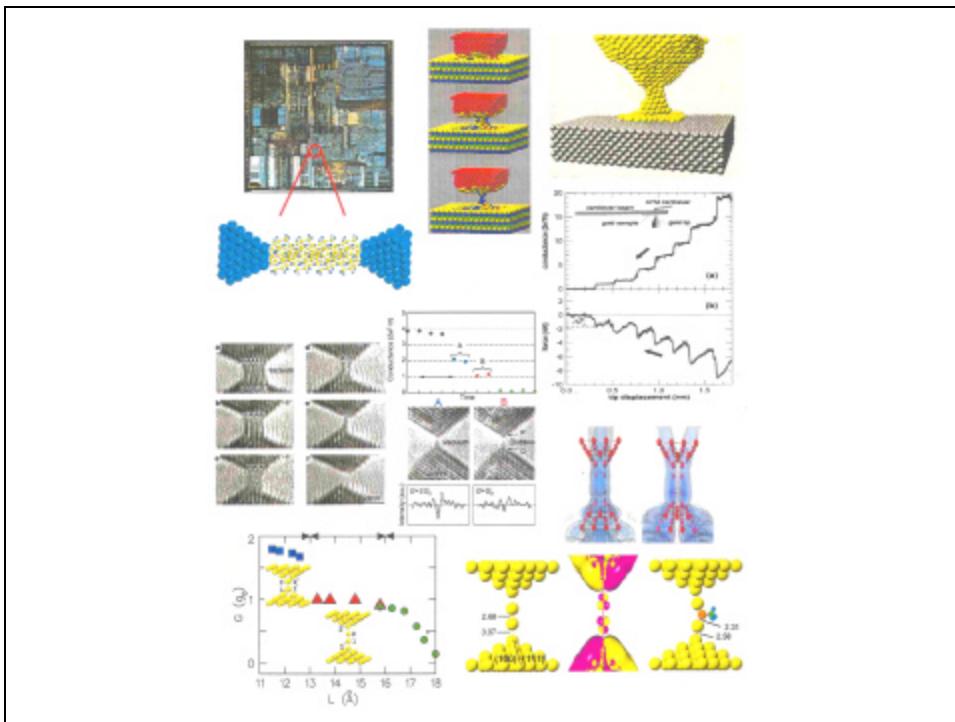
Nanohydrodynamics

Atomistic Simulations as Experiments

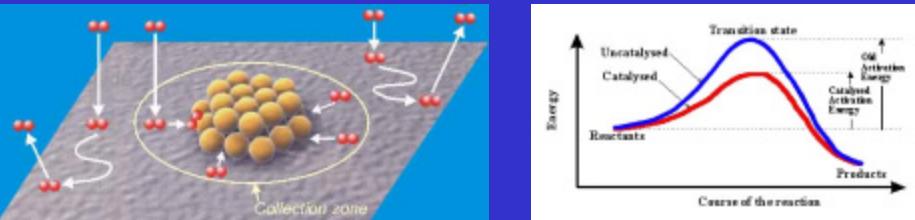
FIXING THE CONTINUUM







Supported Au nano-clusters on metal-oxide (MO) substrates : heterogeneous catalysis



Surprising :

- (a) active at low T < 300 K
- (b) humidity is beneficial
- (c) activity for particles as small as Au₈

Catalytic activity depends on :

- (a) Au charge state
- (b) cluster/surface interface
- (c) cluster morphology
- (d) state of MO substrate

Sanchez *et al.* *J. Phys. Chem. A* 103, 9573 (1999) ; Yoon *et. al.* *Science* (2005)

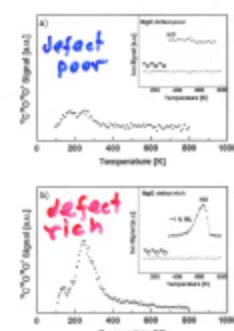
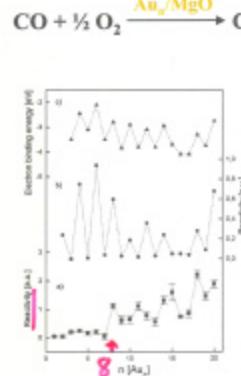
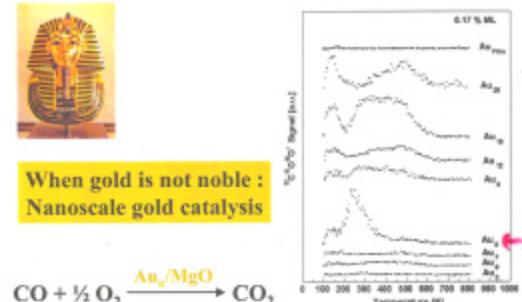
Heiz & Landman, NANOCATALYSIS
(Springer, Berlin, 2006)

**U.Heiz, W.-D.
Schneider,
U. Landman *et. al***
J. Phys. Chem. A (1999)

**NANOCATALYSIS
HEIZ & LANDMAN
(SPRINGER, 2006)**

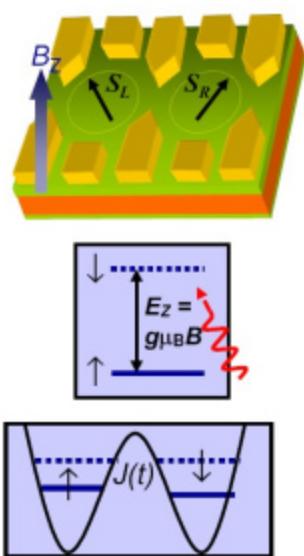


When gold is not noble :
Nanoscale gold catalysis



EXOTIC STATES OF MATTER

BOSONS AND FERMIONS CONFINED IN TRAPS AND QUANTUM DOTS

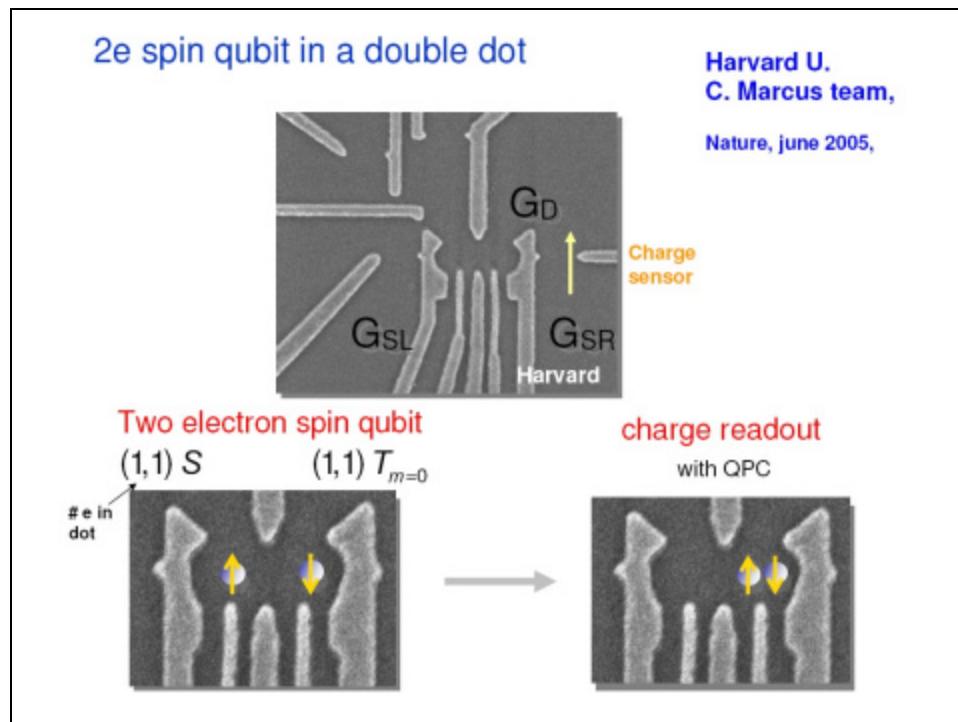
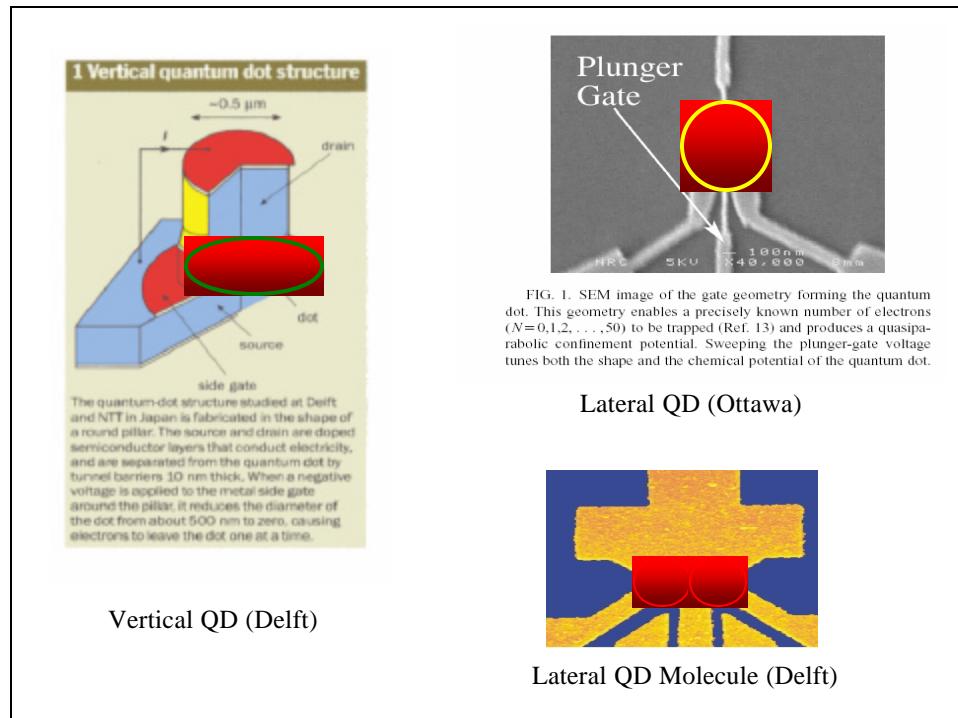


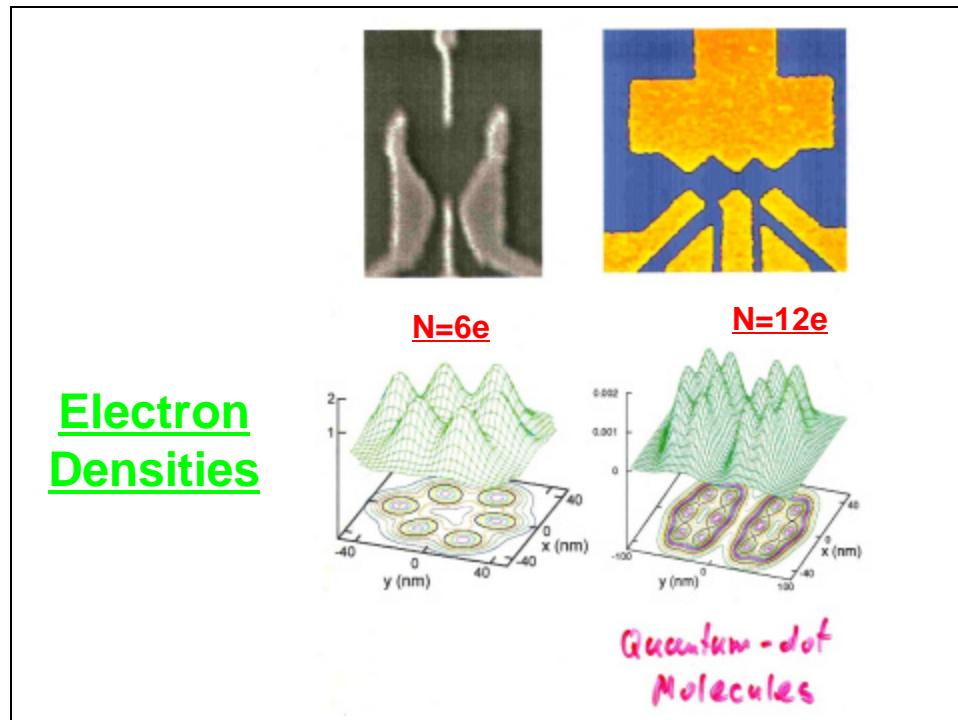
B2) Spin qubits

Initial ideas: Loss & DiVincenzo (1998)

- 1-qubit control:
 - magnetic (ESR)
 - electric (modulate effective g-factor)
- 2-qubit coupling:
exchange interaction between 2 dots
- *Read-out through charge*

Expts: TU Delft , Harvard





Wigner Crystals

DECEMBER 1, 1934 PHYSICAL REVIEW VOLUME 46

On the Interaction of Electrons in Metals

E. Wigner, *Princeton University*
(Received October 15, 1934)

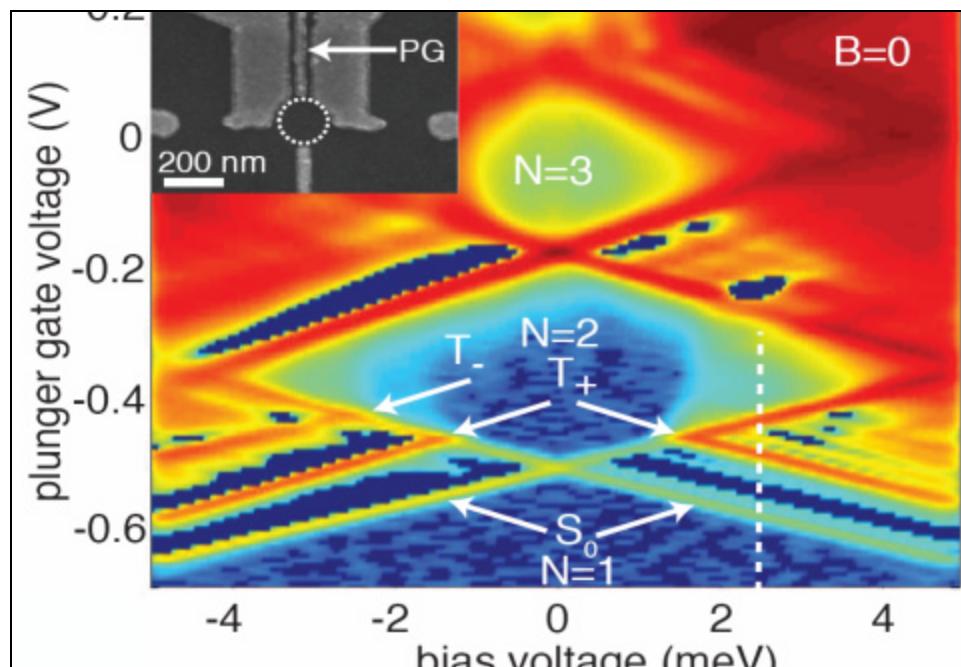
The energy of interaction between free electrons in an electron gas is considered. The interaction energy of electrons with parallel spin is known to be that of the space charges plus the exchange integrals, and these terms modify the shape of the wave functions but slightly. The interaction of the electrons with antiparallel spin, contains, in addition to the interaction of uniformly distributed space charges, another term. This term is due to the fact that the electrons repel each other and try to keep as far apart as possible. The total energy of the system will be decreased through the corresponding modification of the wave function. In the present paper it is attempted to calculate this "correlation energy" by an approximation method which is, essentially, a development of the energy by means of the Rayleigh-Schrödinger perturbation theory in a power series of ρ .

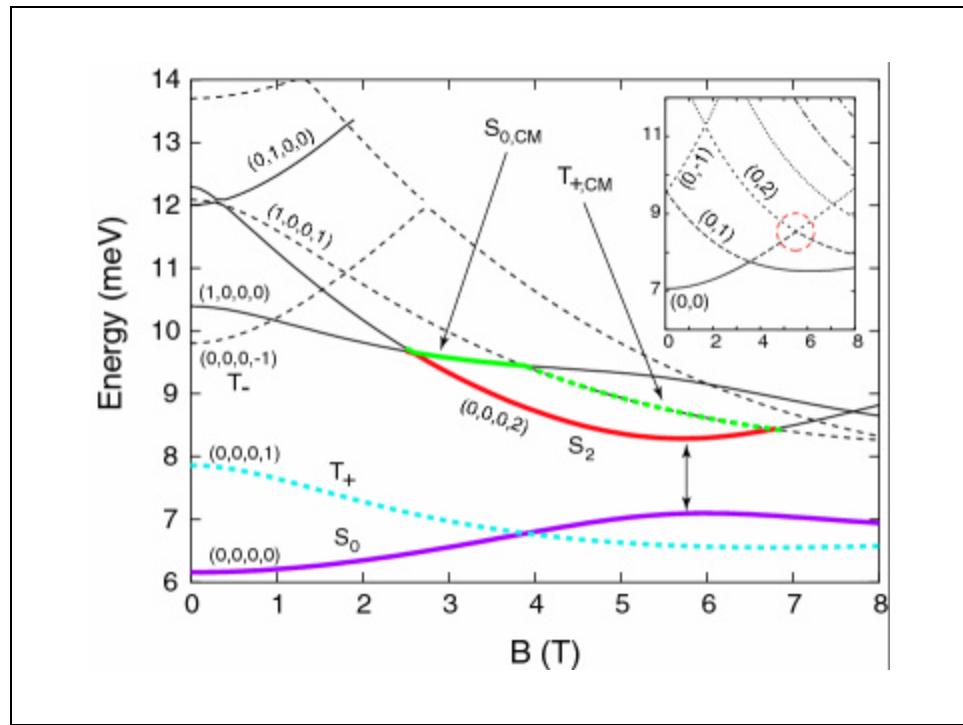
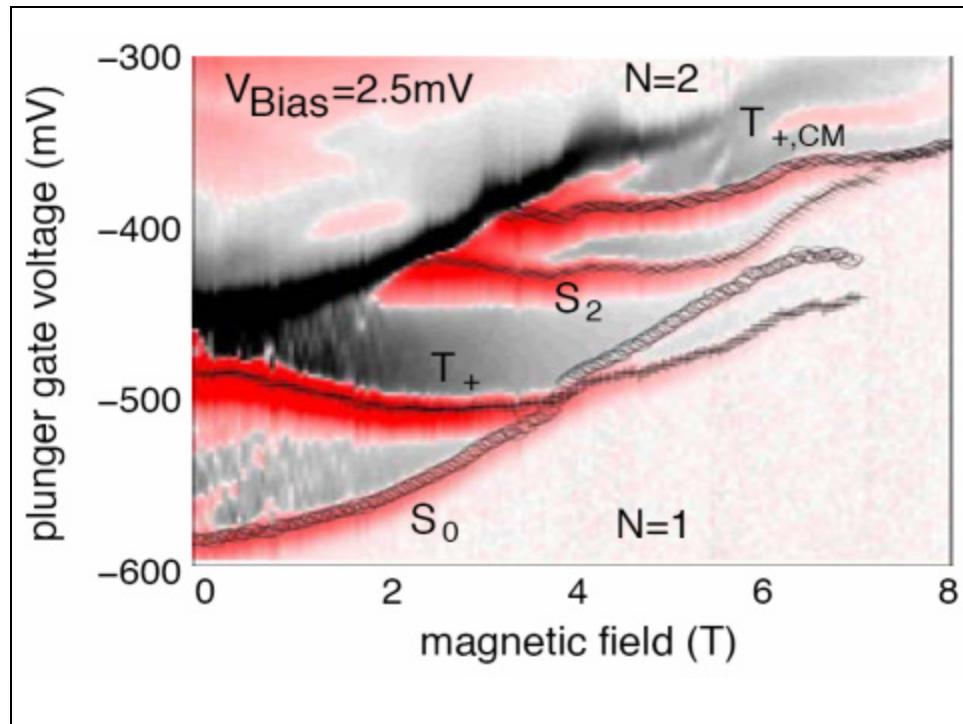


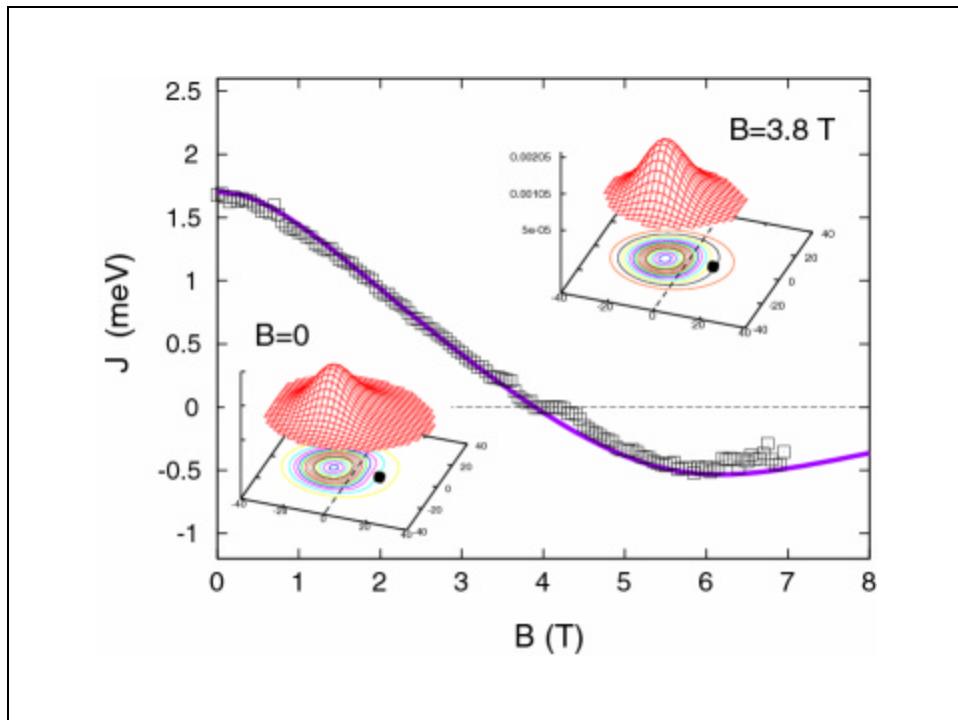
"If the electrons had no kinetic energy, they settle in configurations which correspond to the absolute minima of the potential energy. These are **close-packed lattice configurations**, with energies very near to that of the body-centered lattice ... "

***Excitations of 2e correlated electrons
in a lateral quantum dot with negligible
zeeman splitting***

*C. Ellenberger, T. Ihn, K. Enslin, C.
Yannouleas, Uzi Landman, D. Driscoll, A.C.
Gossard,
Phys. Rev. Lett. 96, 126806 (2006).*







Crystalline phases of bosons in rotating traps: Tonks-Girardeau gas on a ring

Phys. Rev. Lett. 93, 230405 (2004)

Phys. Rev. Lett. 97, 090401 (2006)

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REPORTS

Observation of a One-Dimensional Tonks-Girardeau Gas

Toshiya Kinoshita, Trevor Wenger, David S. Weiss*

We report the observation of a one-dimensional (1D) Tonks-Girardeau (TG) gas of bosons moving freely in 1D. Although TG gas bosons are strongly interacting, they behave very much like noninteracting fermions. We enter the TG regime with cold rubidium-87 atoms by trapping them with a combination of two light traps. By changing the trap intensities, and hence the atomic interaction strength, the atoms can be made to act either like a Bose-Einstein condensate or like a TG gas. We measure the total 1D energy and the length of the gas. With no free parameters and over a wide range of coupling strengths, our data fit the exact solution for the ground state of a 1D Bose gas.

At zero temperature, dense, weakly interacting bosons in a 1D trap form a Bose-Einstein condensate (BEC) (*I*). Dilute, strongly interacting bosons in 1D, however, act in a completely different manner. Rather than condensing into a single quantum state, they are expected to repel each other, as if they were noninteracting fermions (*2*, *3*). Known as a Tonks-Girardeau (TG) gas

tion of a 1D lattice, the spatially modulated atoms can be described as quasiparticles with increased effective mass (*24*). In this way, a system with $\gamma = 0.5$ can be interpreted as having $\gamma_{\text{eff}} \sim 200$. The measured momentum distributions in such a system were found to fit well to a modified theoretical result derived for the lattice TG gas (*24*).

We create a 1D gas with no periodic

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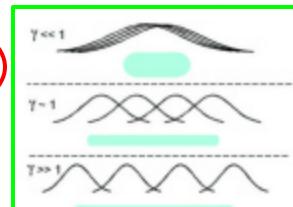


Fig. 1. Cartoon of 1D atom distributions. In each of three γ regimes, the upper drawing illustrates the size, ℓ , and separation, r , of single-particle wave functions. As γ increases, ℓ becomes smaller and r becomes larger, until the bosons, like fermions, become spatially distinct. The three shaded drawings below represent the atomic density in a 1D tube. In our experiment, γ is changed by transversely squeezing the tube. For $\gamma \ll 1$, the gas acts like a fluid and expands axially when squeezed transversely. As γ rises, transverse squeezing has less of an axial effect. For $\gamma \gg 1$, deep in the TG regime, transverse squeezing has no effect on the axial distribution for energy.

tively tightly confined in two transverse dimensions, and loosely confined in an av-

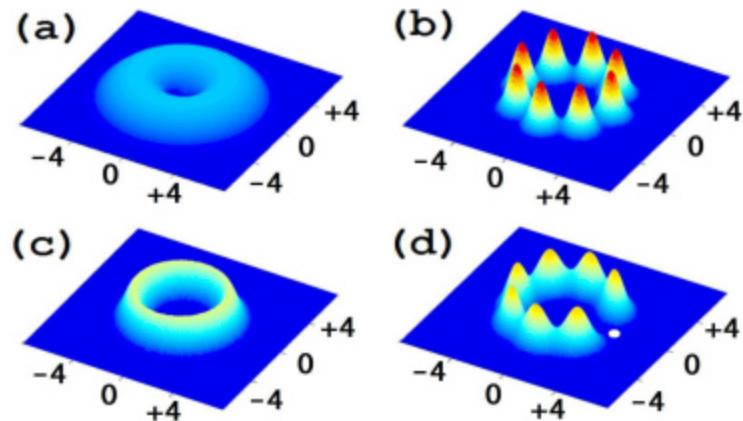
Summary.

harmonic trap	ring trap ($r_0=3$)
$\gamma=50$ $\gamma=0$ $L_z=0$	$\gamma=50$ $\gamma=0.2$ $r_0=3$ $L_z=16$

(PRL 93, 230405 (2004)).

Hidden crystalline structure of ground state is revealed via stepwise variation of angular momentum of ground state (in steps of N or $N-1$)

Eight bosons in rotating trap.



***The Scientist is not the person
who always gives the
right answers,
he is
one who asks the
right questions***

Claude Levi- Strauss (1908-)

THE
END