Title: Simulations of complex materials across multiple length scales

Date: May 10, 2006 02:00 PM

URL: http://pirsa.org/06050004

Abstract: A variety of physical phenomena involve multiple length and time scales. Some interesting examples of multiple-scale phenomena are: (a) the mechanical behavior of crystals and in particular the interplay of chemistry and mechanical stress in determining the macroscopic brittle or ductile response of solids; (b) the molecular-scale forces at interfaces and their effect in macroscopic phenomena like wetting and friction; (c) the alteration of the structure and electronic properties of macromolecular systems due to external forces, as in stretched DNA nanowires or carbon nanotubes. In these complex physical systems, the changes in bonding and atomic configurations at the microscopic, atomic level have profound effects on the macroscopic properties, be they of mechanical or electrical nature. Linking the processes at the two extremes of the length scale spectrum is the only means of achieving a deeper understanding of these phenomena and, ultimately, of being able to control them. While methodologies for describing the physics at a single scale are well developed in many fields of physics, chemistry or engineering, methodologies that couple scales remain a challenge, both from the conceptual point as well as from the computational point. In this presentation I will discuss the development of methodologies for simulations across disparate length scales with the aim of obtaining a detailed description of complex phenomena of the type described above. I will also present illustrative examples, including hydrogen embrittlement of metals, DNA conductivity and translocation through nanopores, and affecting the wettability of surfaces by surface chemical modification.

Simulations of Complex Materials Across Multiple Scales

Simulations of Complex Materials Across Multiple Scales

- Methodologies for mutliscale simulations
- Brittle vs. Ductile: the effects of chemistry on mechanical behavior
- Hydro-philic/phobic behavior of surfaces
- DNA translocation through nanopores

14,400 setae/mm^2

50-gram gecko uses 0.04% of its setae to walk on wall

"How gecko toes stick"
Kellar Autumn
Am. Sci. **94** (2006)

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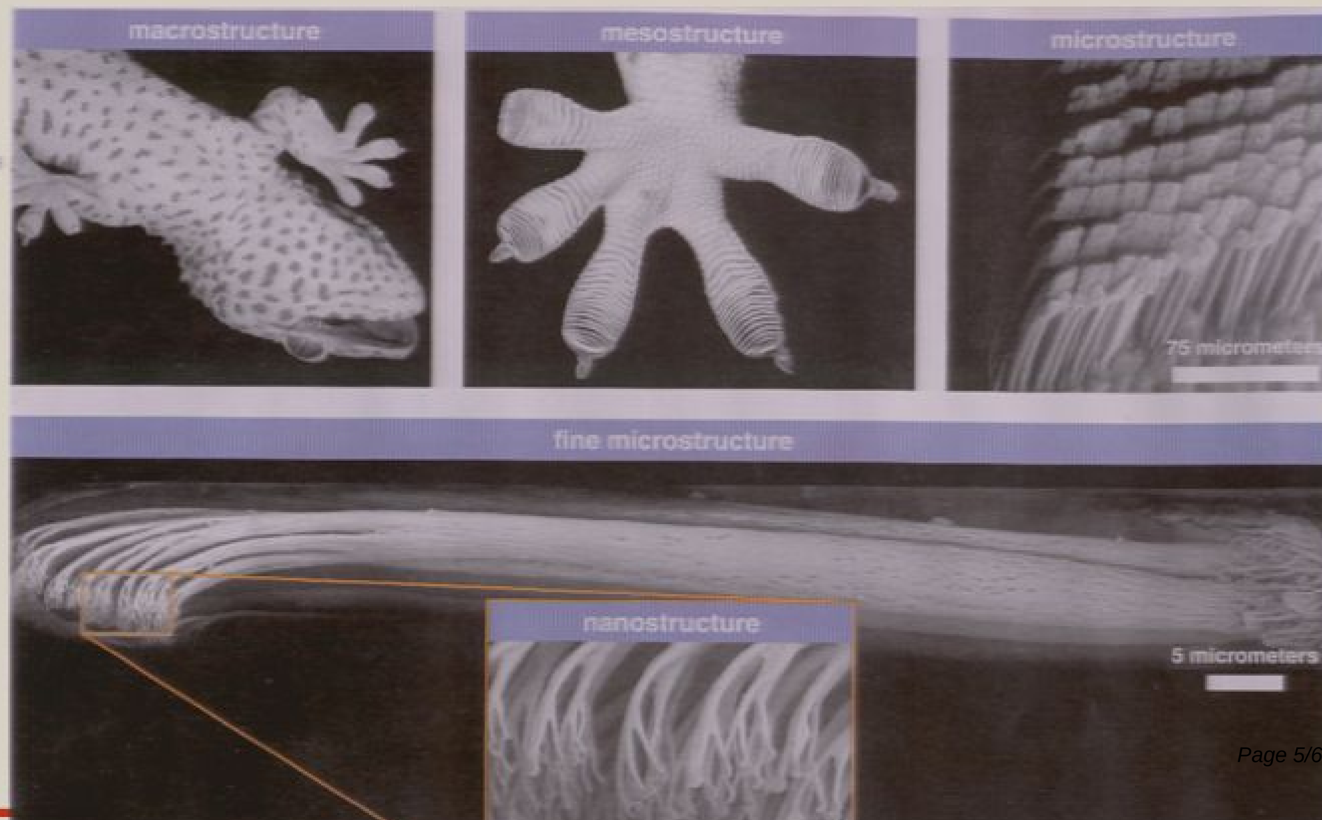

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low gecko toes stick“
Kellar Autumn
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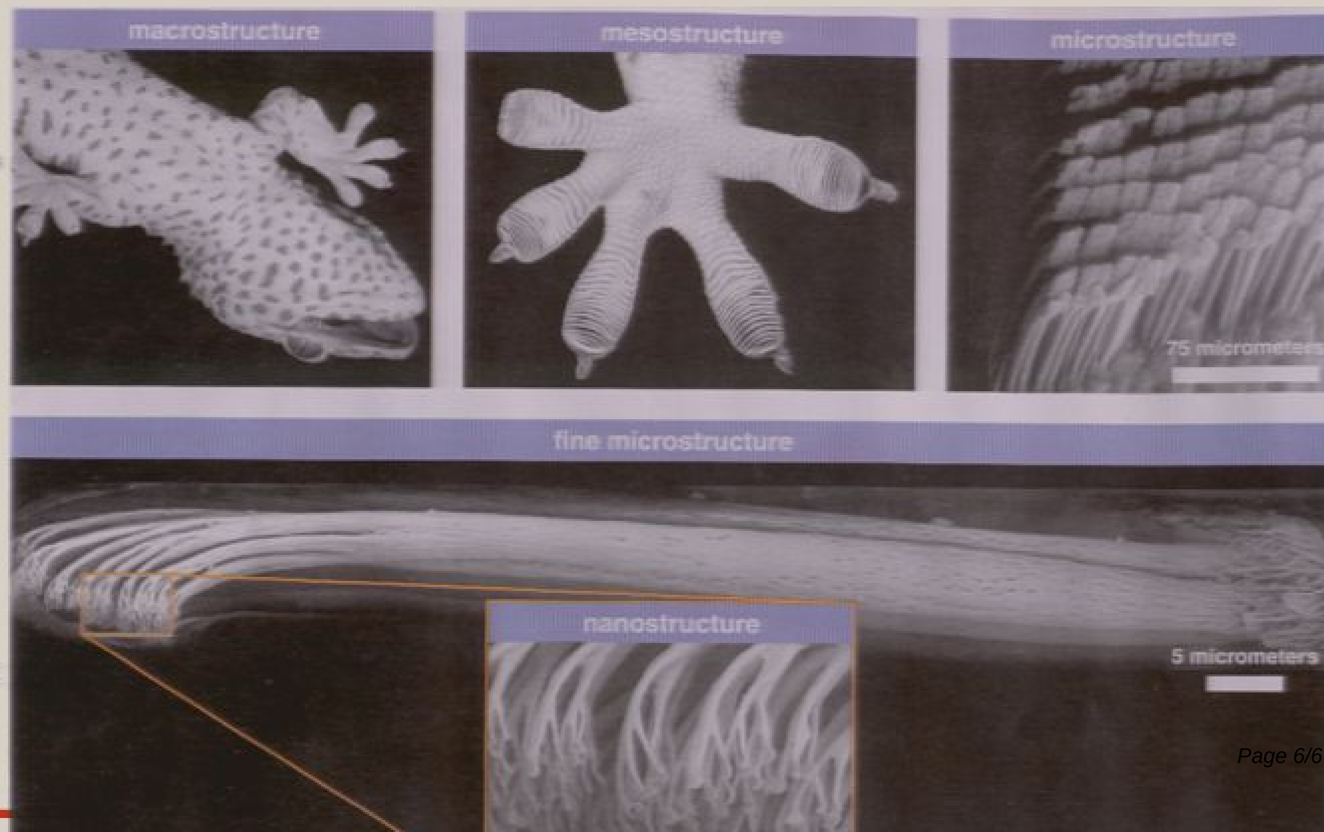
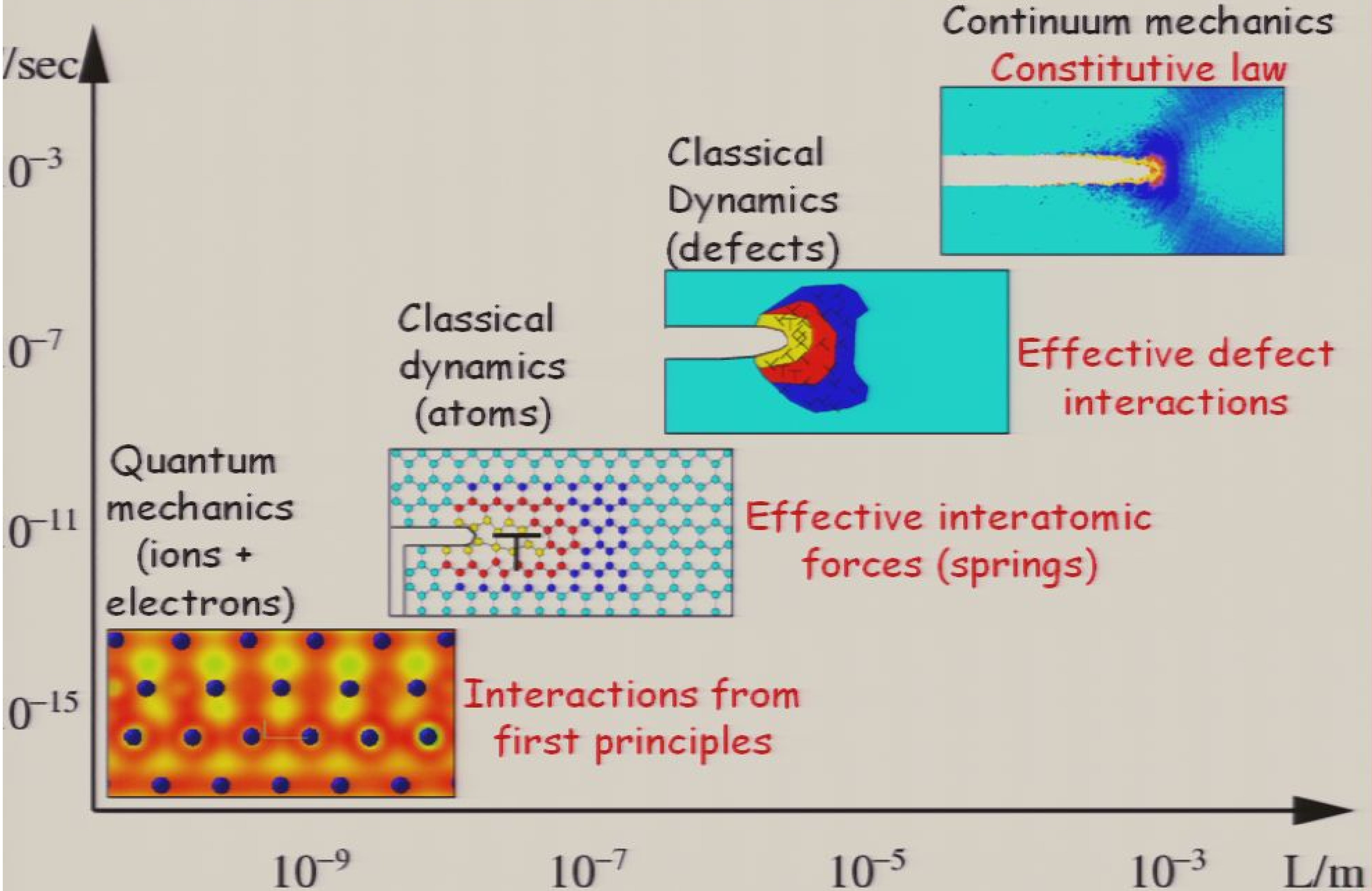


apillary forces?
IO: setal surfaces
re super-hydrophobic
contact angle 160°)

Multiple length scales: crack propagation



Multiscale simulations for materials:

- Sequential: "message" passing
  - scales weakly coupled
  - complete knowledge of relevant processes at each scale

  (*e.g. growth on surfaces*)

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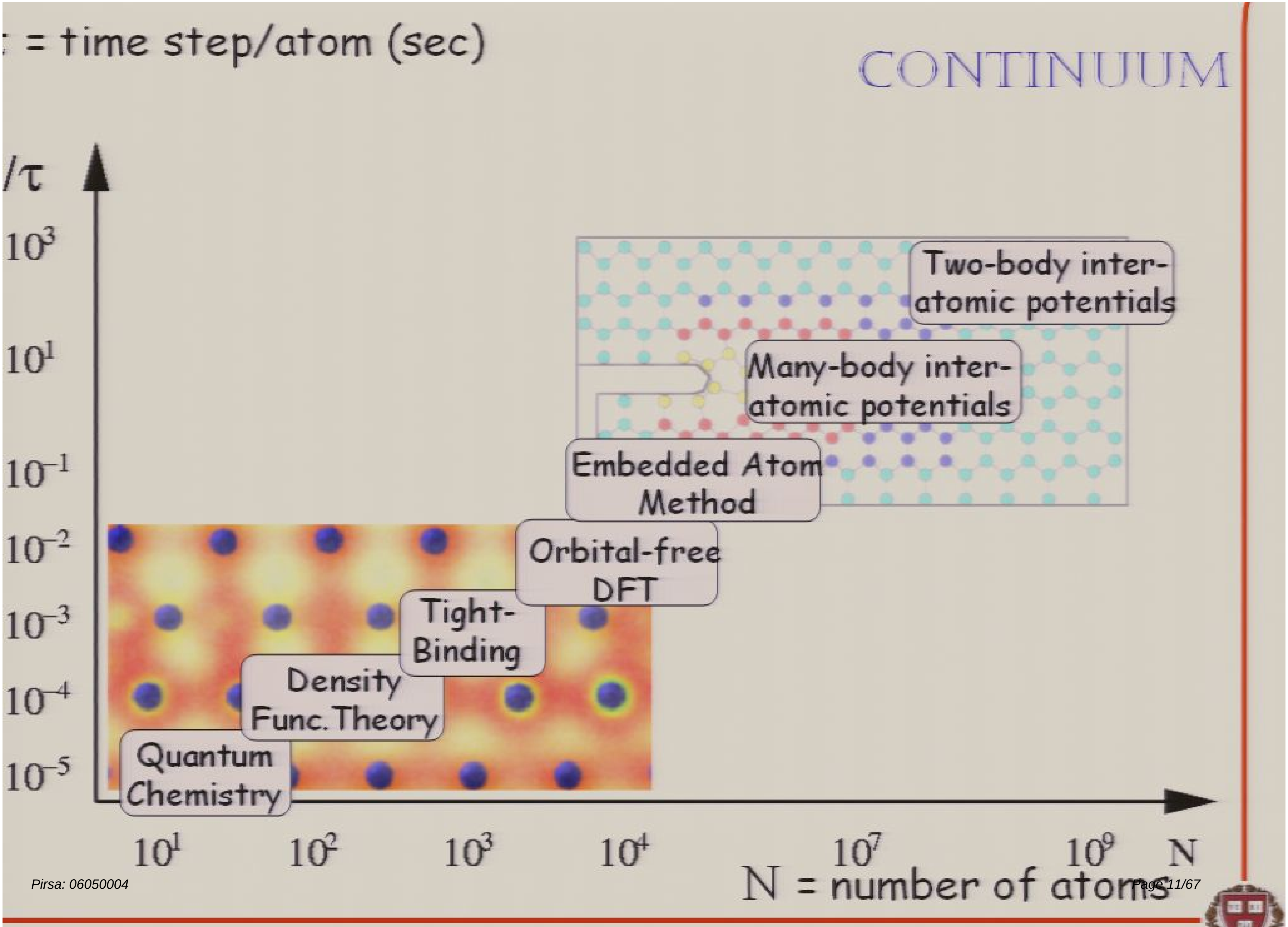
Recent review: G. Lu and E. Kaxiras, *Handbook for Theoretical and Computational Nanotechnology (2005)*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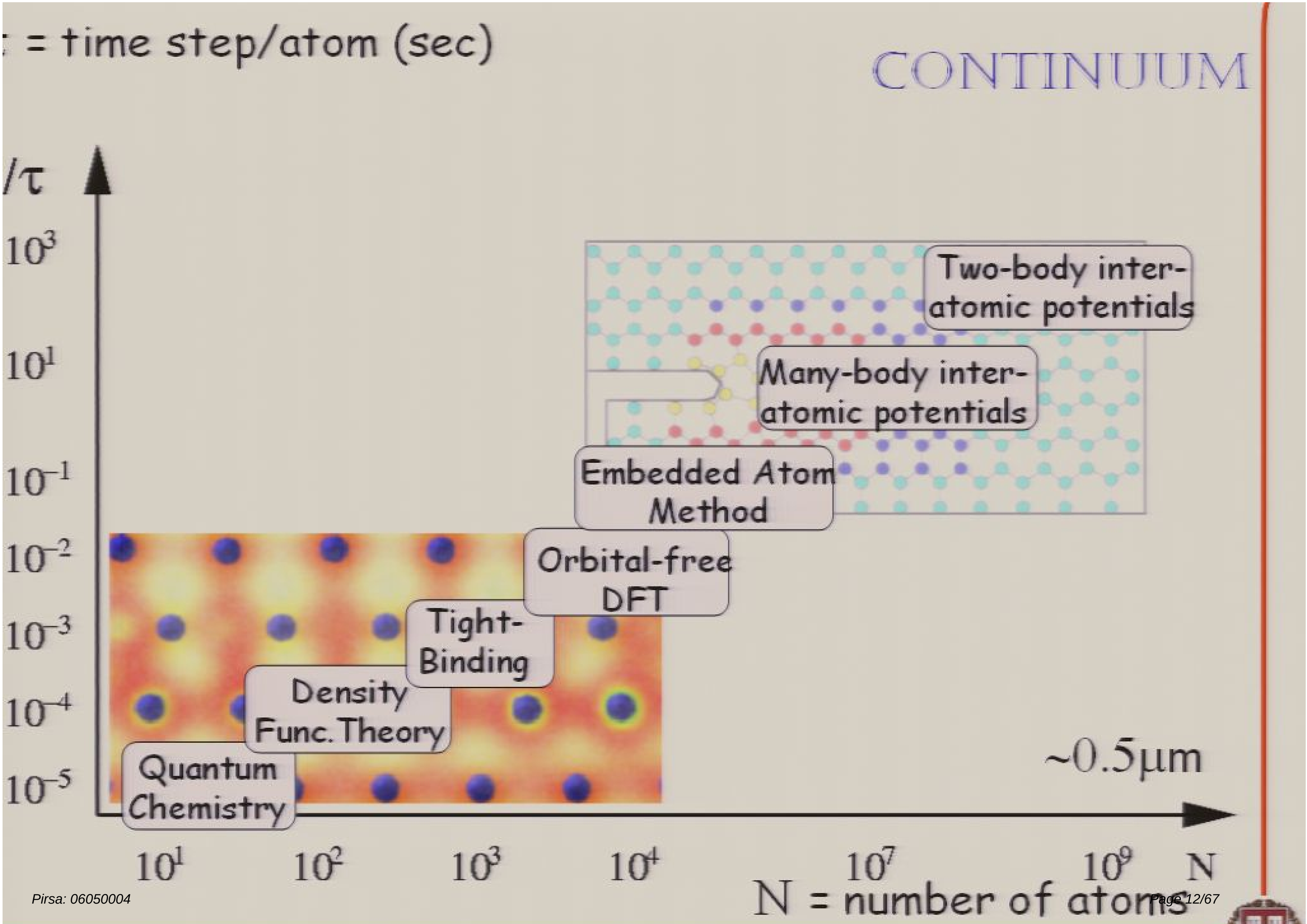
CONTINUUM
/τ
10^3
10^1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
Two-body inter-atomic potentials
Many-body inter-atomic potentials
Embedded Atom Method
Orbital-free DFT
Tight-Binding
Density Func. Theory
Quantum Chemistry
10^1
10^2
10^3
10^4
10^7
10^9
N
N = number of atoms



: = time step/atom (sec)
CONTINUUM
/τ
10³
10¹
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
Two-body inter-atomic potentials
Many-body inter-atomic potentials
Embedded Atom Method
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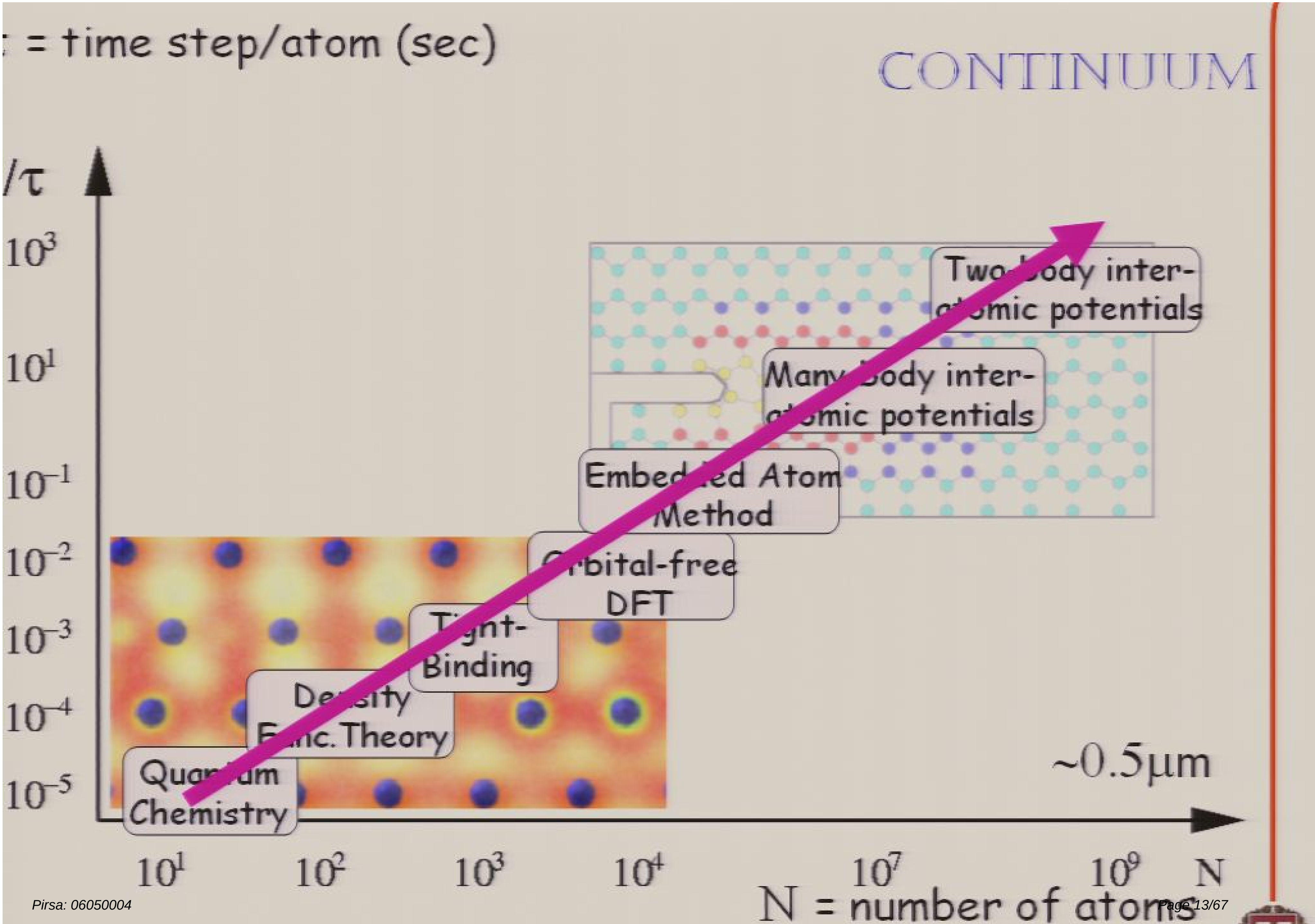
~0.5μm
10¹
10²
10³
10⁴
10⁷
10⁹
N
N = number of atoms



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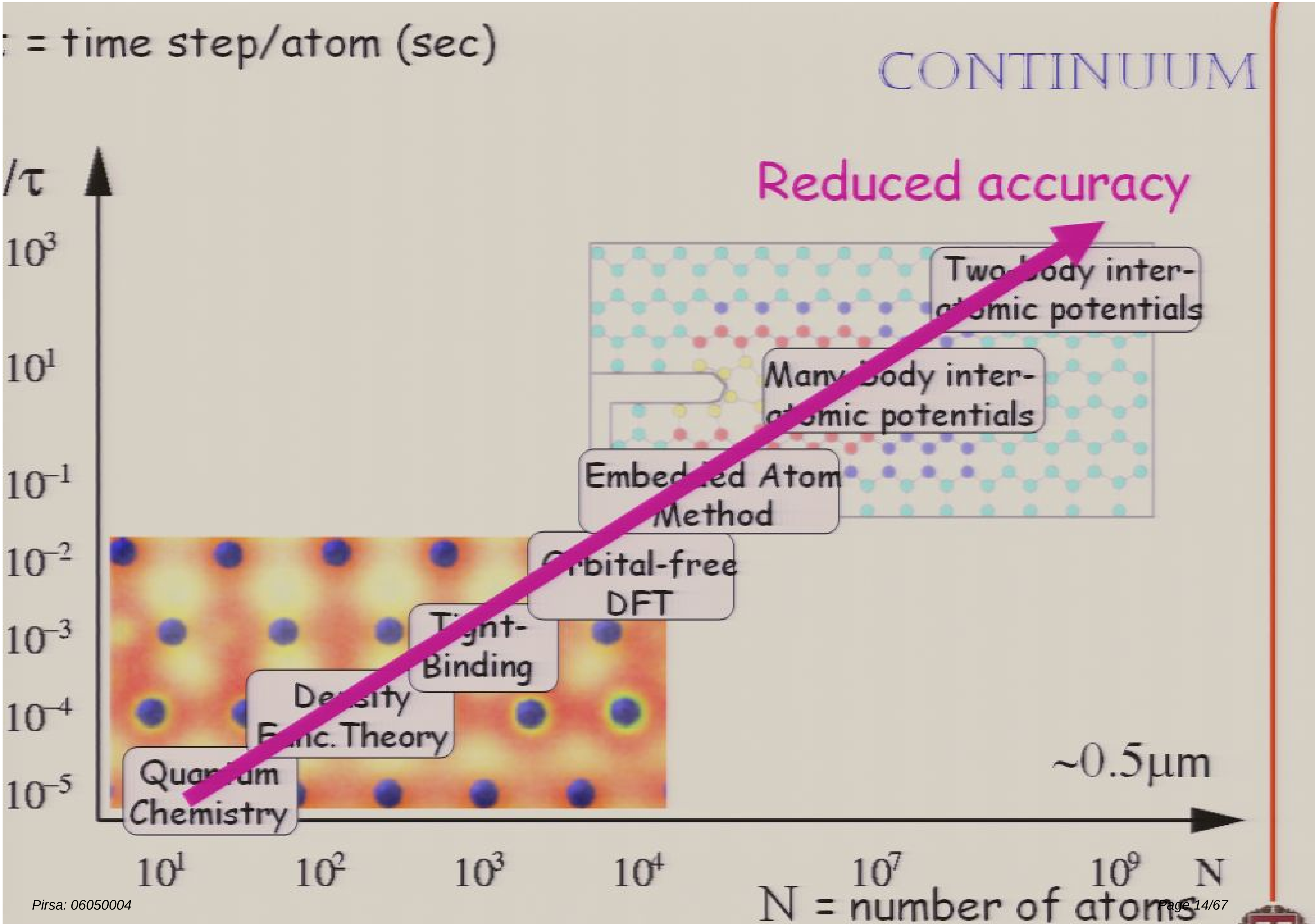
= time step/atom (sec)
CONTINUUM
/τ
Reduced accuracy
10^3
10^1
10^-1
10^-2
10^-3
10^-4
10^-5
Two-body inter-atomic potentials
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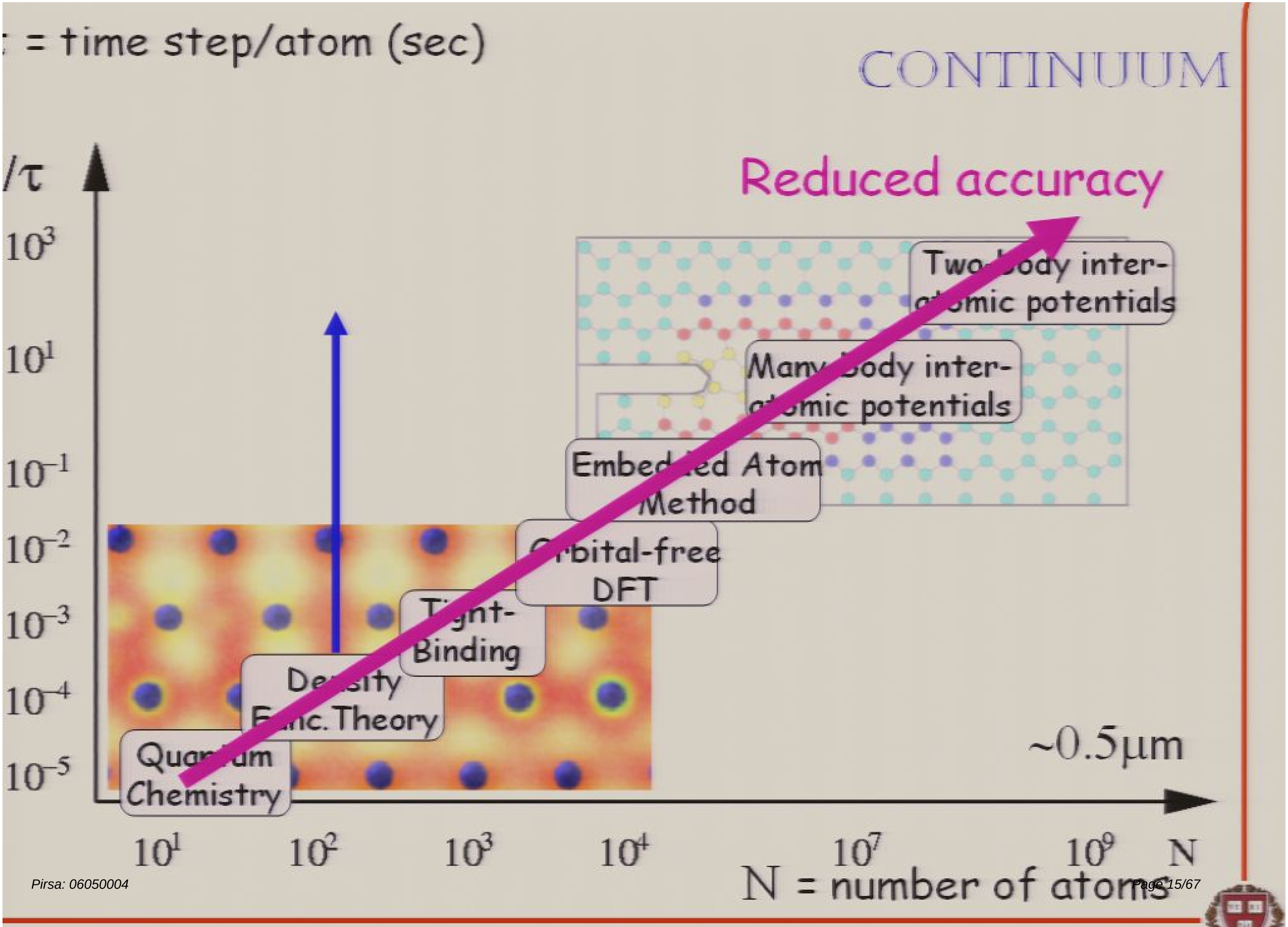
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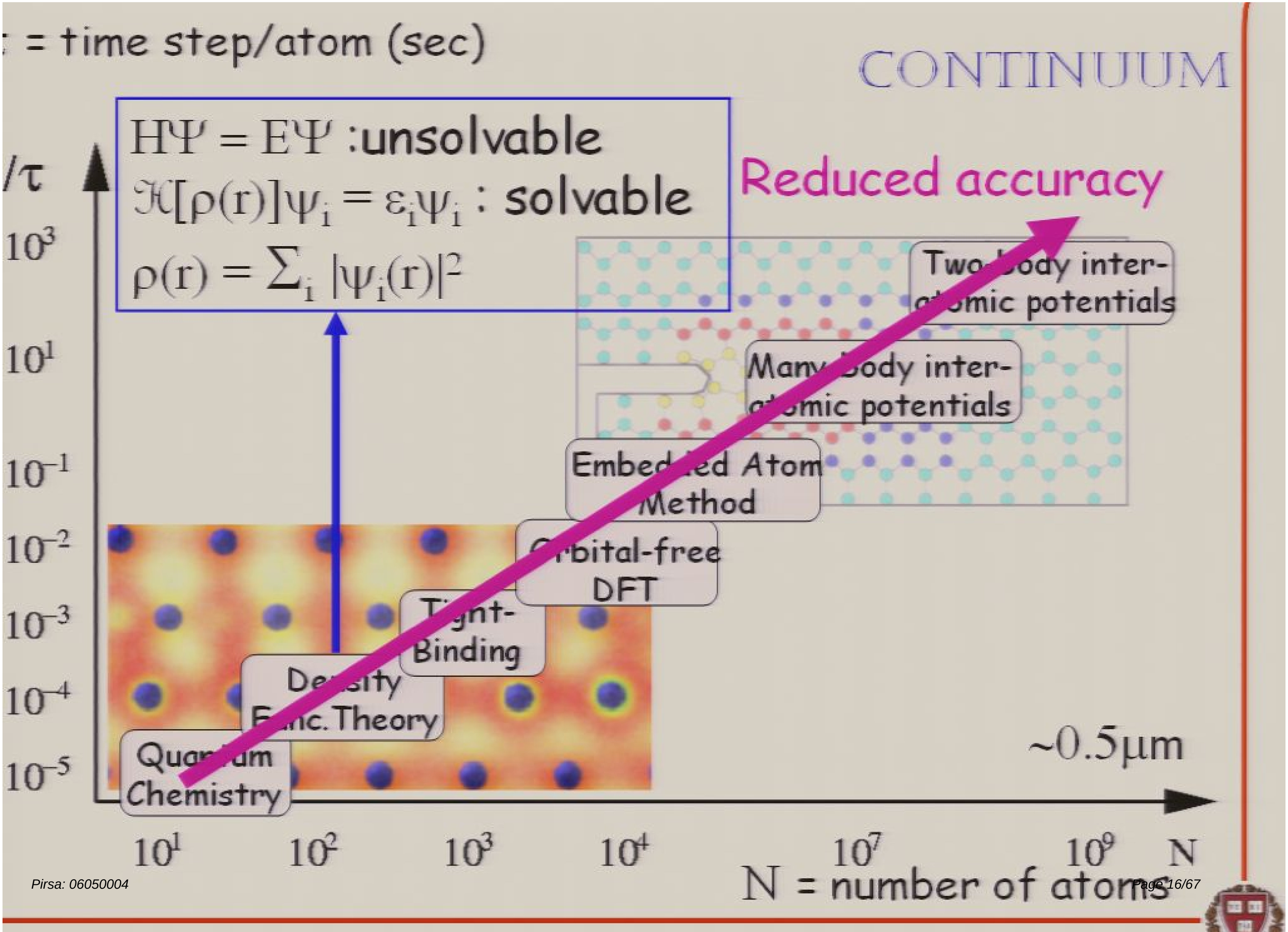

τ = time step/atom (sec)
CONTINUUM
HΨ = EΨ :unsolvable
ℋ[ρ(r)]ψi = εiψi : solvable
ρ(r) = Σi |ψi(r)|2
Reduced accuracy
1/τ
103
101
10−1
10−2
10−3
10−4
10−5
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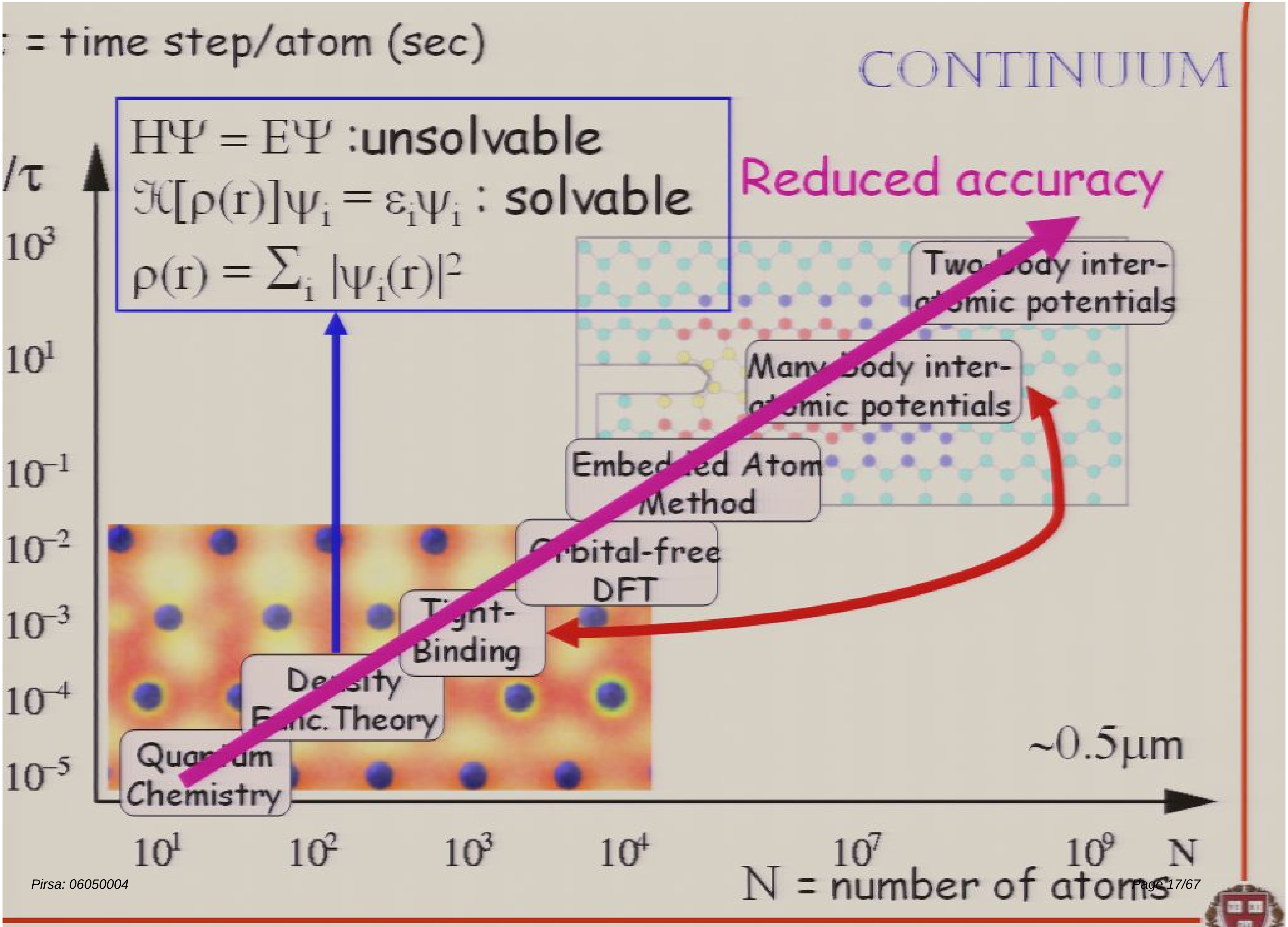
~0.5μm
101
102
103
104
107
109
N
N = number of atoms



τ = time step/atom (sec)
CONTINUUM
$H\Psi = E\Psi$:unsolvable
$\mathcal{H}[\rho(r)]\psi_i = \varepsilon_i\psi_i$: solvable
$\rho(r) = \sum_i |\psi_i(r)|^2$
Reduced accuracy
/τ
10^3
10^1
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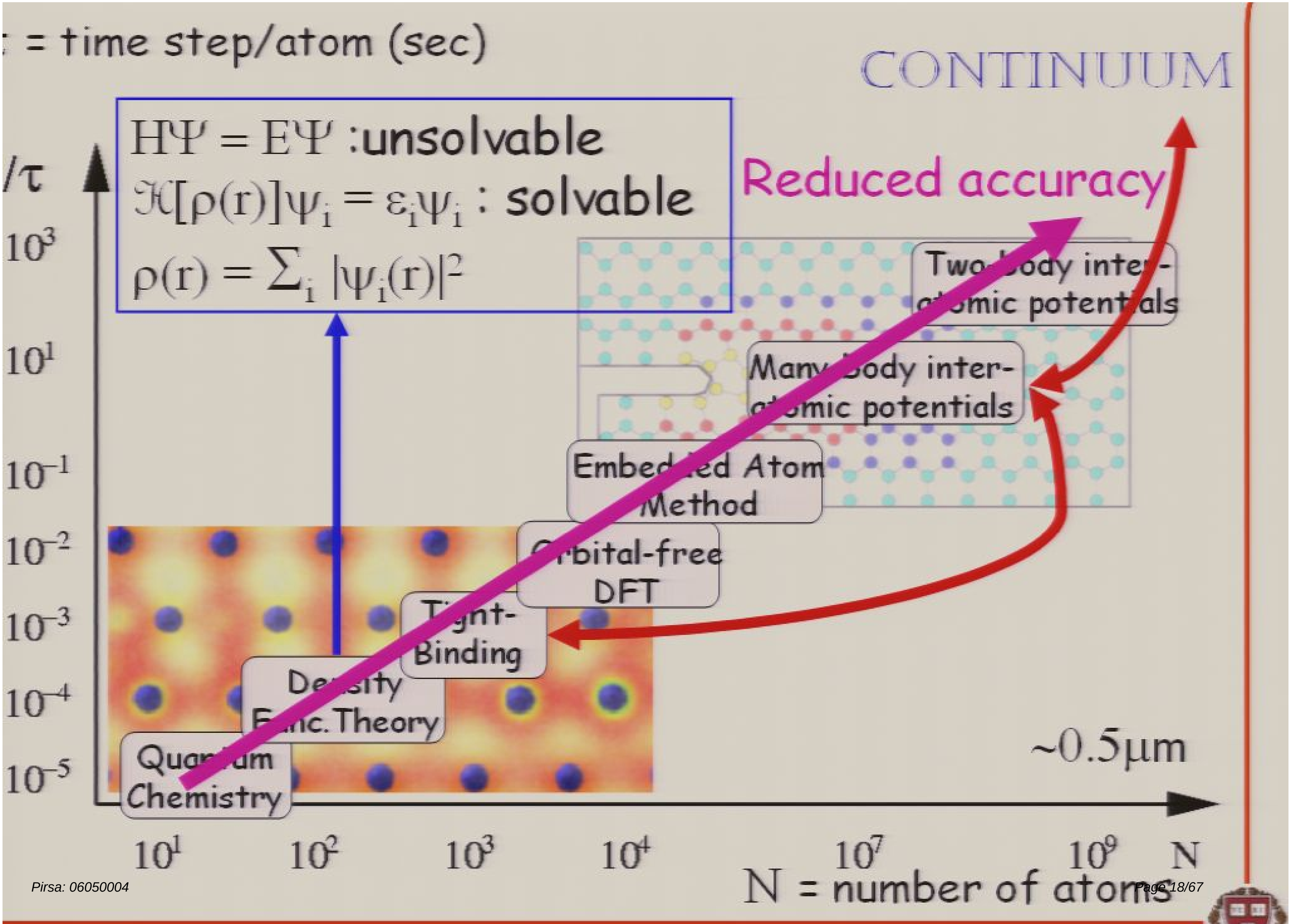

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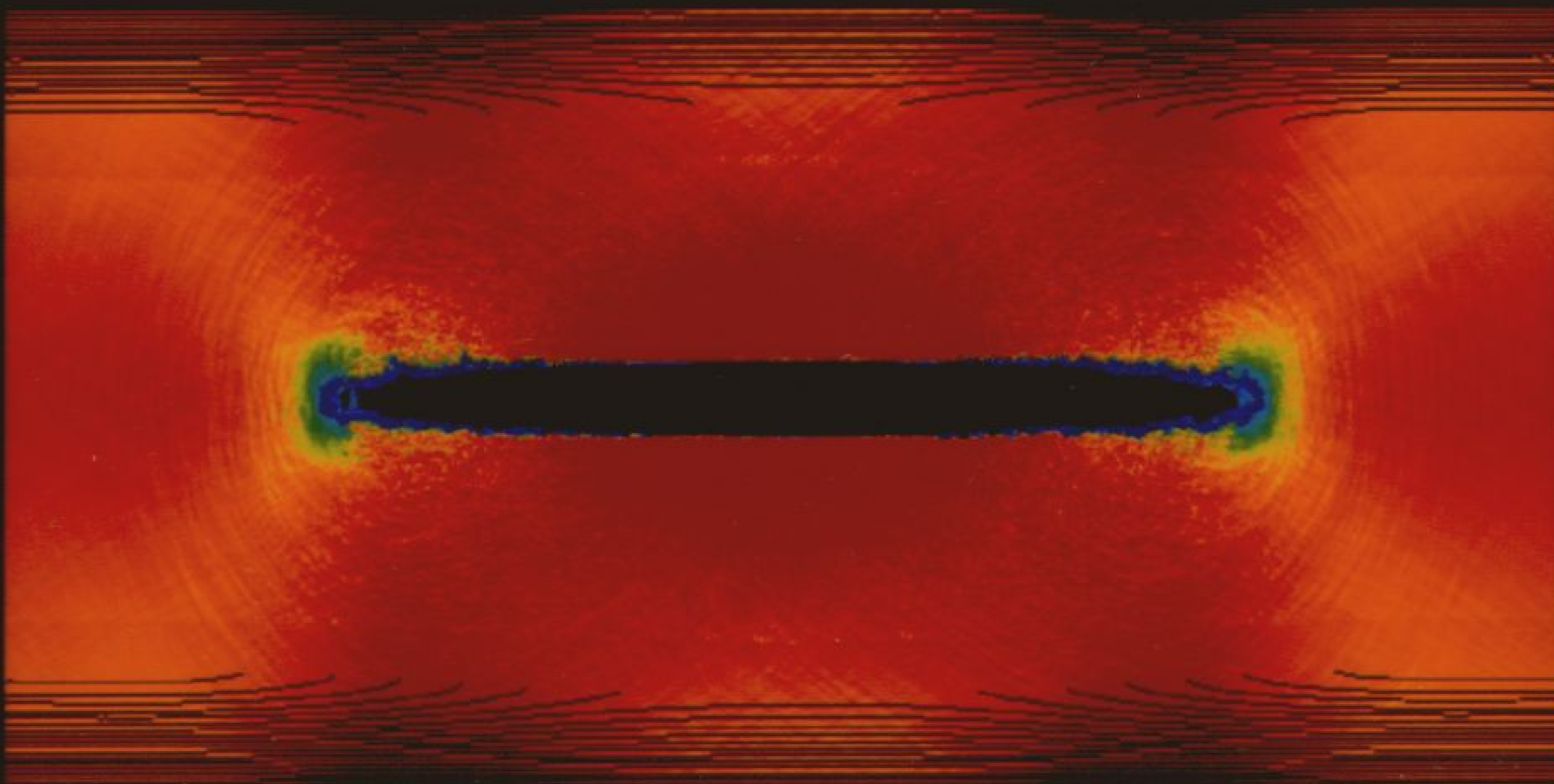
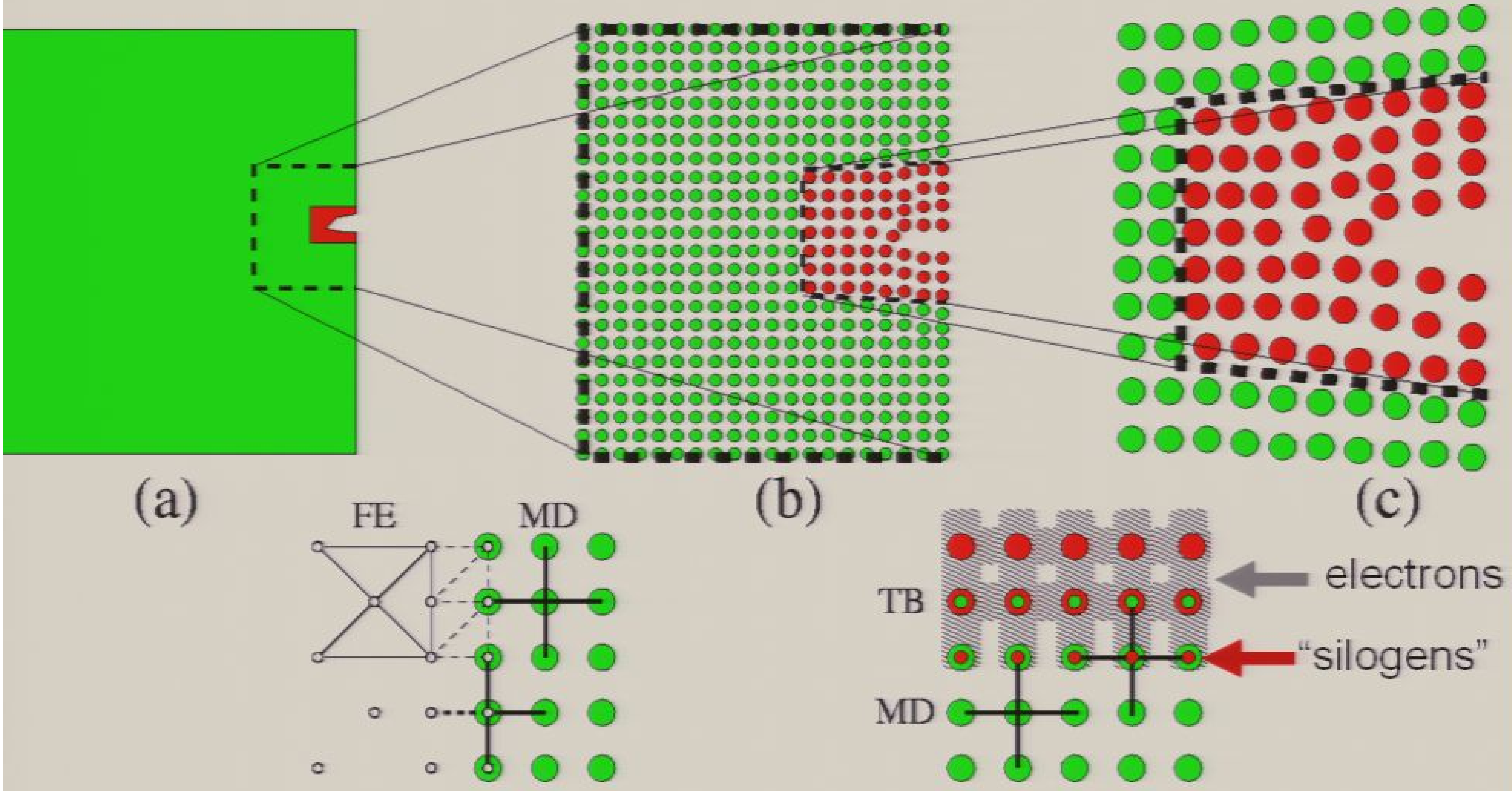
MAAD-Si: no reflection of stress waves, seamless coupling across boundaries



Essentials of the MAAD-Si simulation



F. Abraham, J. Broughton, N. Bernstein, E.K. (Phys. Rev. B, 1998)

Lessons from the MAAD-Si simulation

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- Quantum mechanics (TB) essential in capturing brittle character of Si

  Noam Bernstein *et al.*

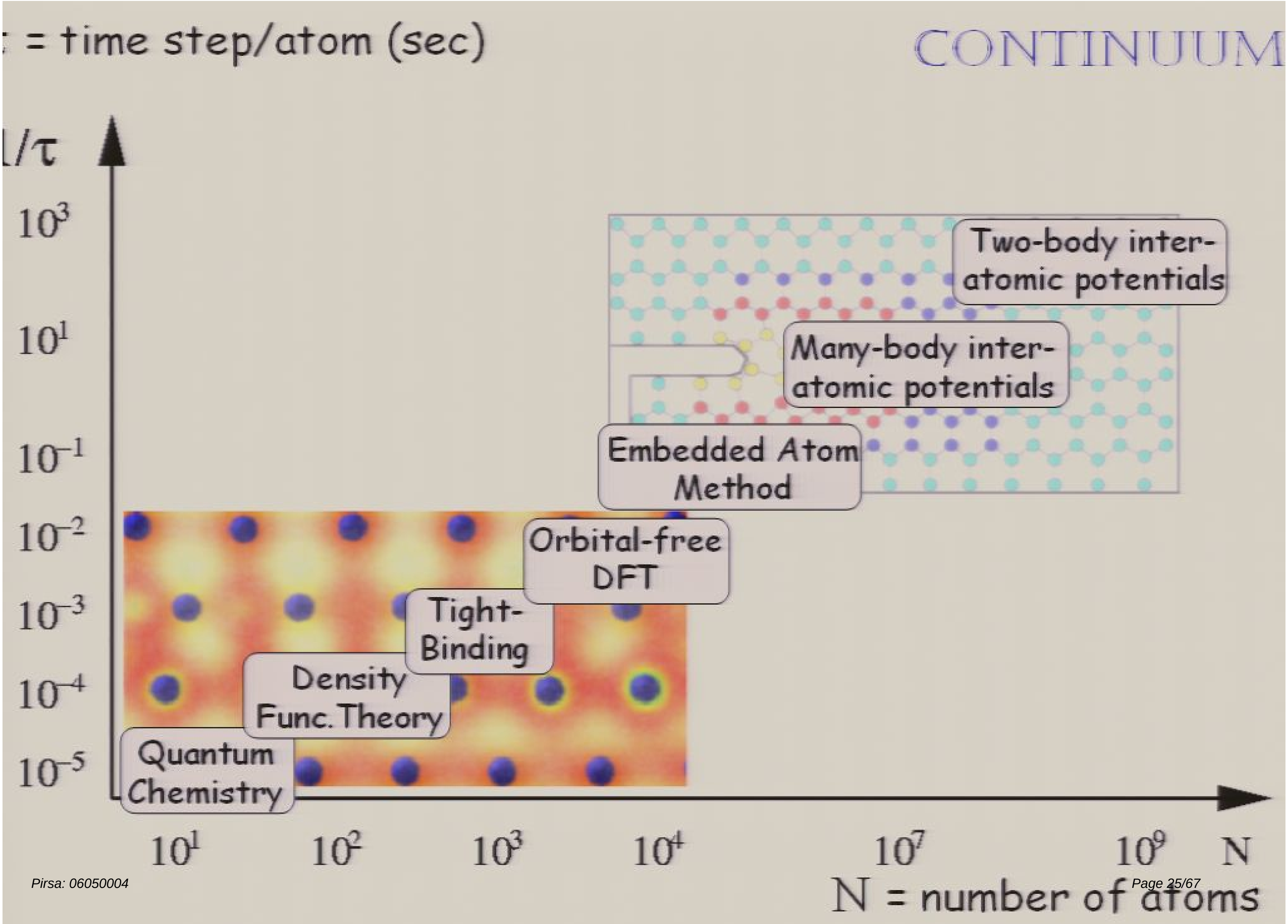
Lessons from the MAAD-Si simulation

- Quantum mechanics (TB) essential in capturing brittle character of Si
  Noam Bernstein *et al.*

- Si is particularly easy to describe in the context of multiscale simulations
  Covalent character of bonds

Metal alloys: change from ductile to brittle behavior induced by chemical impurities

brittle fracture in "hostile" environment (moisture)



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CONTINUUM
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10^3
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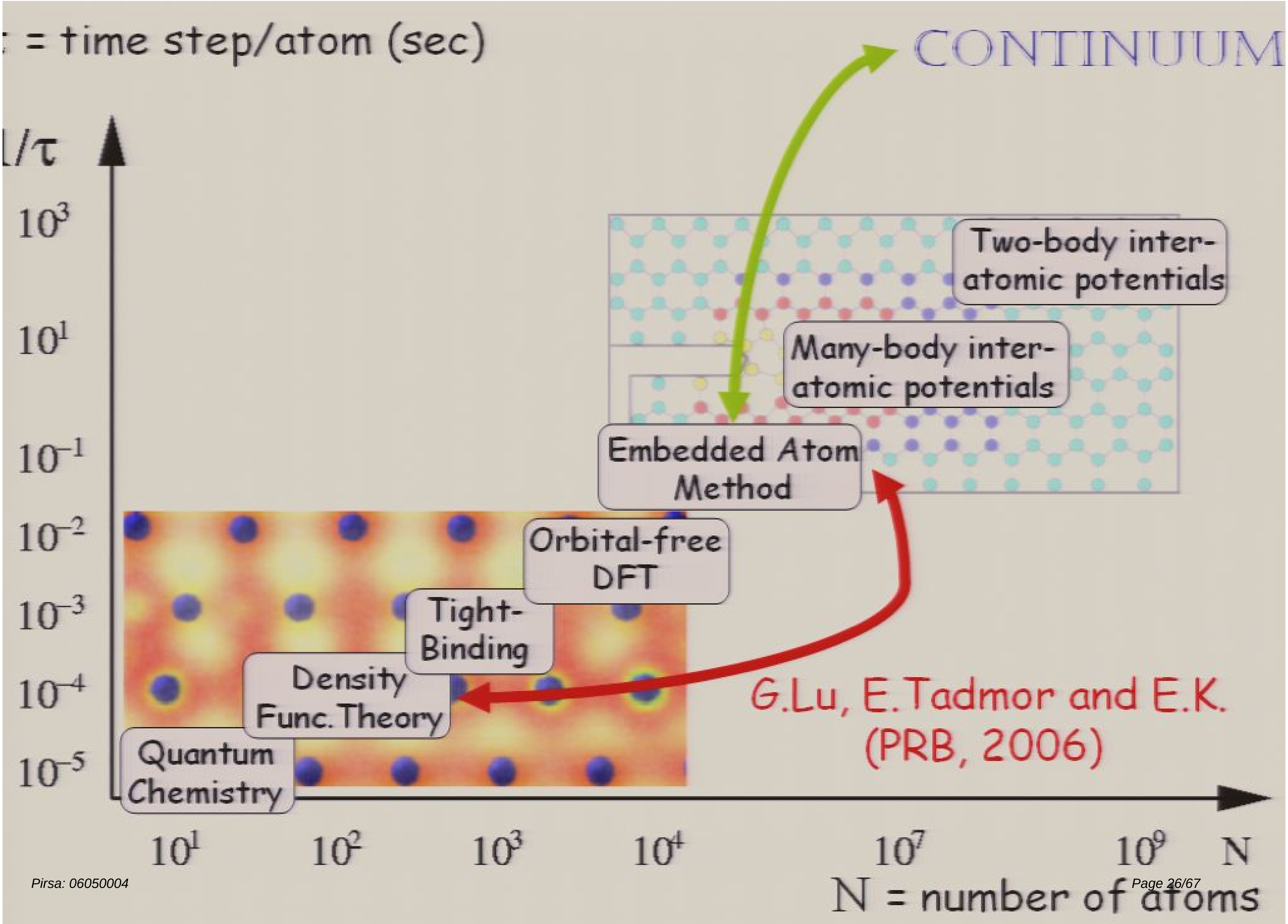
τ = time step/atom (sec)
CONTINUUM
1/τ
10^3
10^1
10^-1
10^-2
10^-3
10^-4
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Quantum Chemistry
G.Lu, E.Tadmor and E.K.
(PRB, 2006)
10^1
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10^3
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10^7
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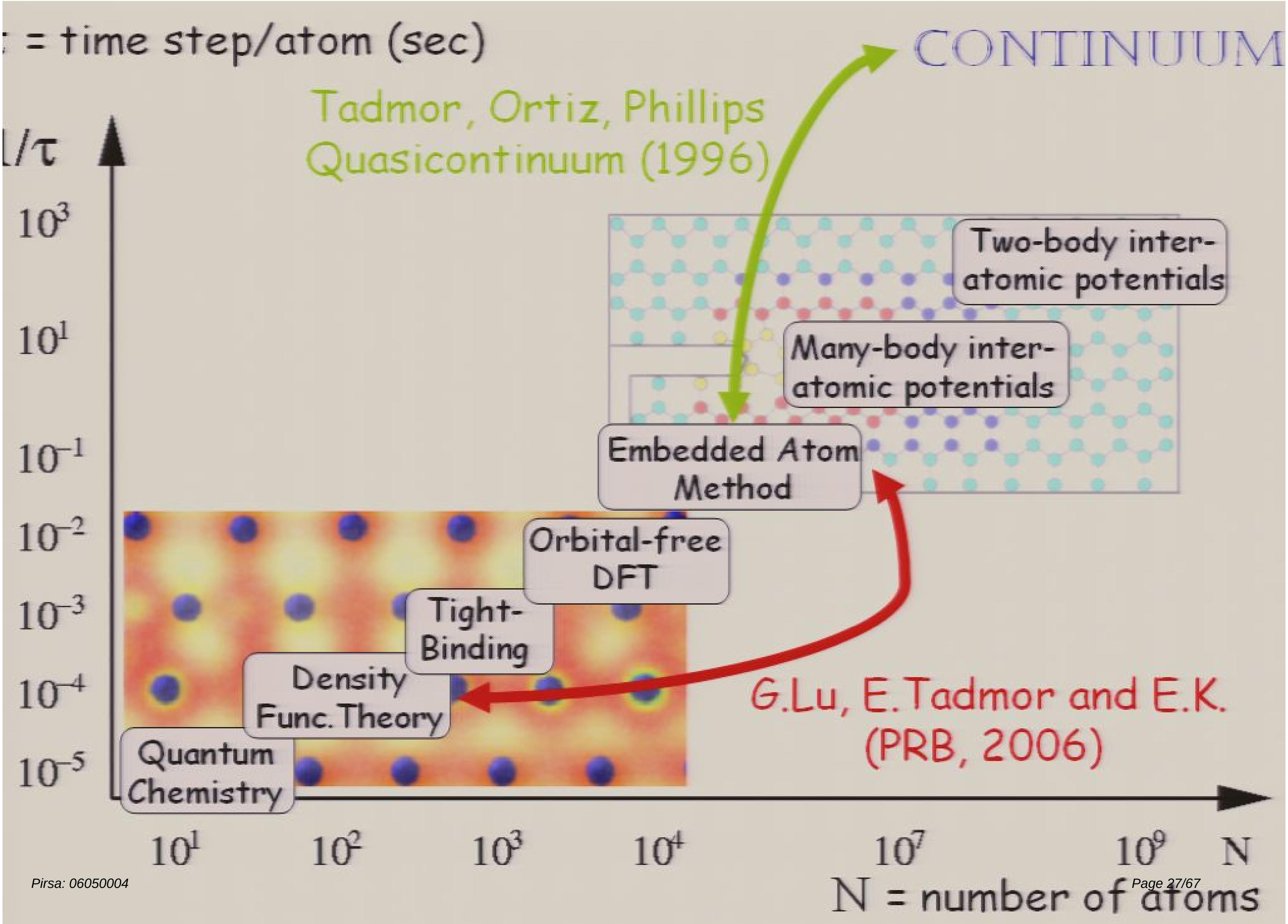
τ = time step/atom (sec)
1/τ
CONTINUUM
Tadmor, Ortiz, Phillips
Quasicontinuum (1996)
10^3
10^1
10^{-1}
10^{-2}
10^{-3}
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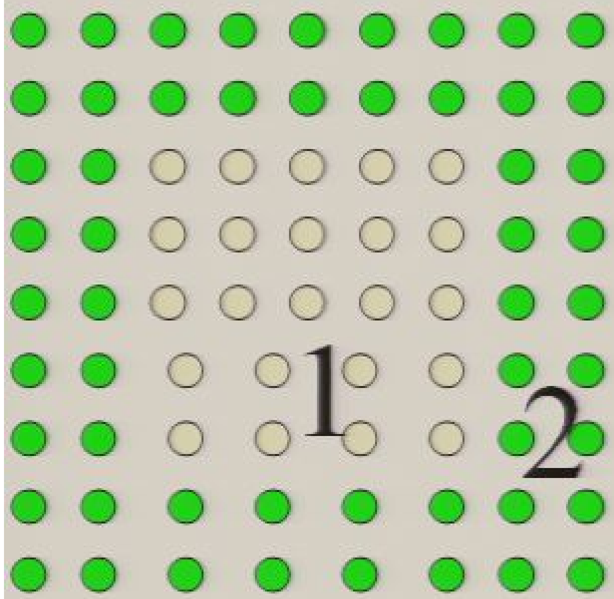
Coupling Formalism



$$E[1+2] = E^{DFT}[1] + E^{EAM}[2] + E^{\text{int}}[1,2]$$

$$E^{\text{int}}[1,2] \equiv E[1+2] - E[1] - E[2]$$

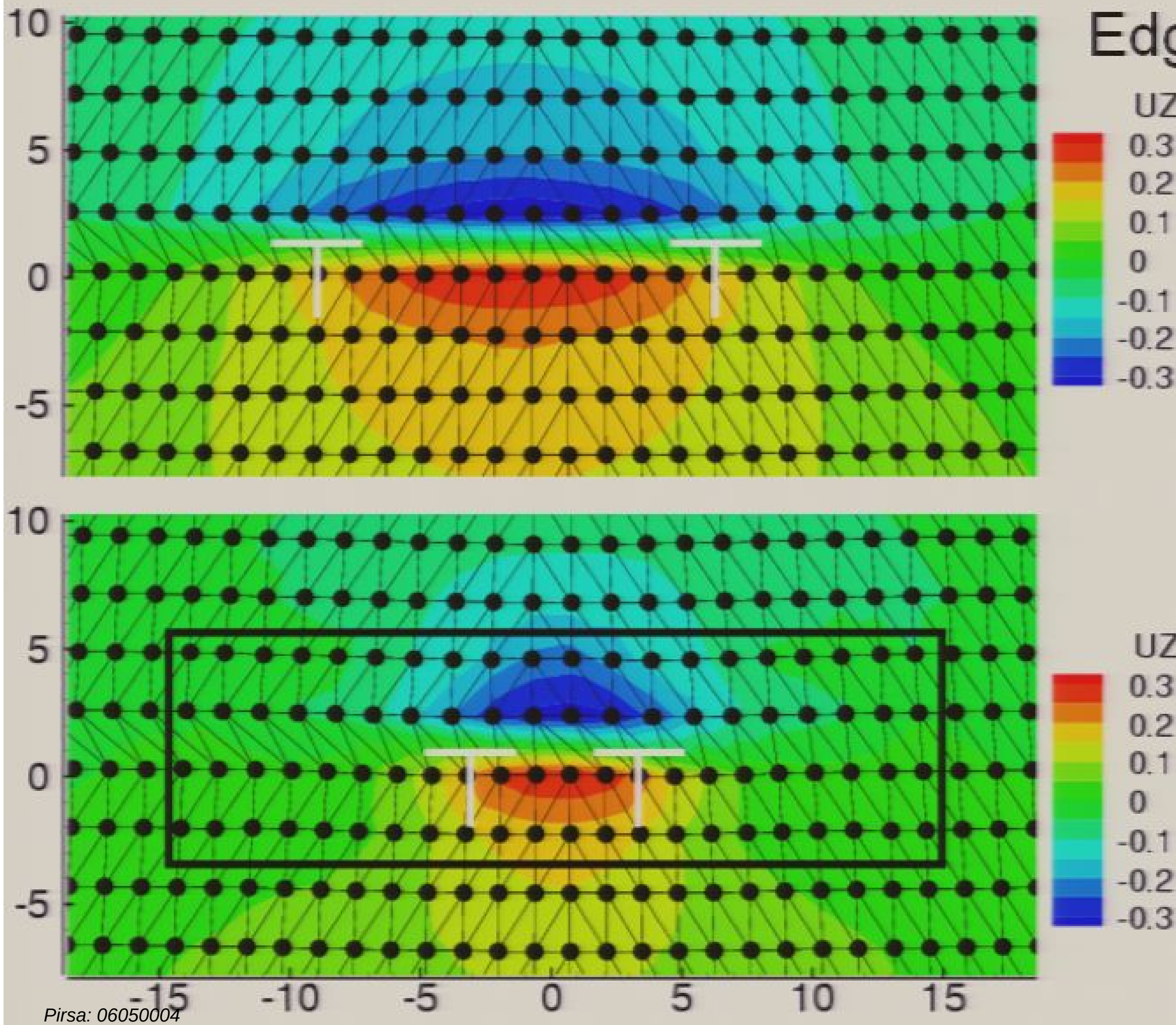
[Wesolowski and Warshel J.Phys.Chem. 1993]

$$\delta E^{int}[1+2] = \delta E^{EAM}[1+2] - \delta E^{EAM}[1] - \delta E^{EAM}[2]$$

only terms on the boundary contribute

- forces inside 1: purely DFT
- forces inside 2: purely EAM
- forces on boundary: EAM+DFT
- (improve by force matching schemes)

Coupling the Quasi-Continuum to DFT

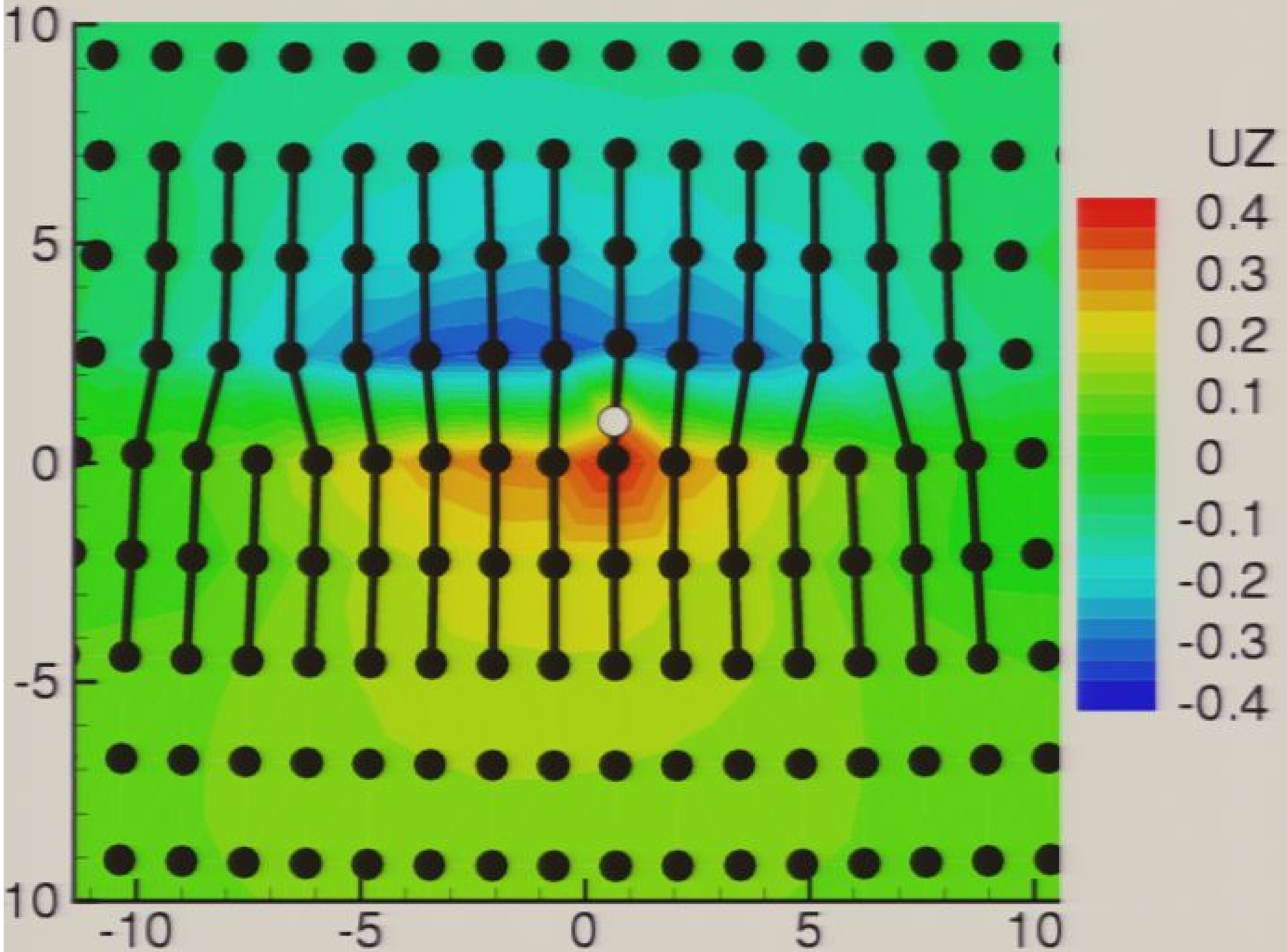


Edge dislocation in Al

QC only (EAM)
Δb = 15.4 Å

QC(EAM) + DFT
Δb = 5.6 Å
(expt. 5.5 Å)

Edge dislocation in Al with H impurities

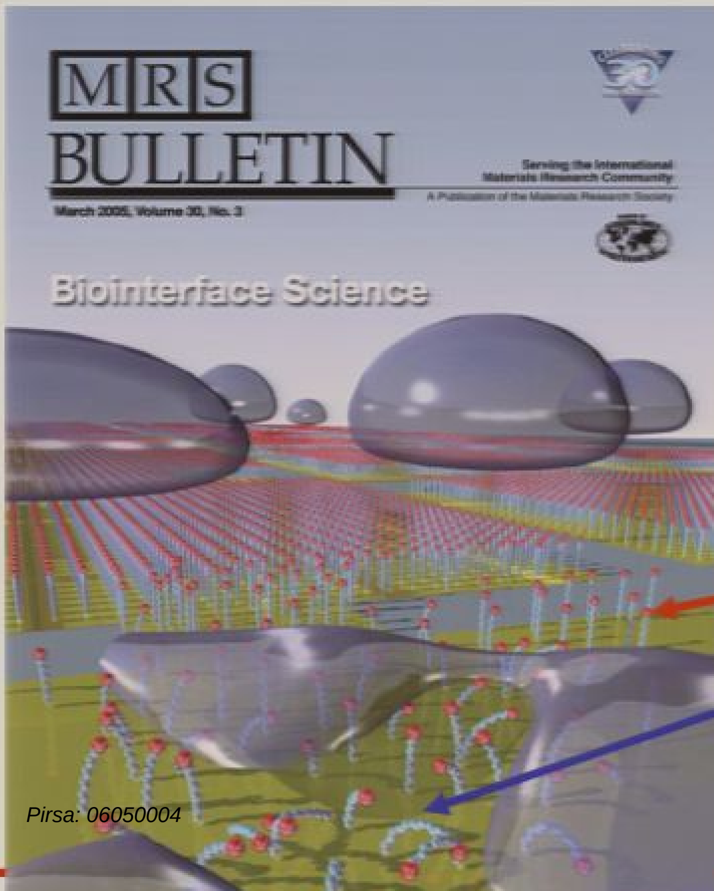


QC(EAM) + DFT
$\Delta b = 13$ Å

H lowers stacking fault energy: wider dislocation consistent with H-embrittlement by enhanced local plasticity mechanism

Tuning the wettability of solid surfaces from (super)hydrophobic to (super)hydrophilic

with Sheng Meng (UT Austin and Harvard)
Zhenyu Zhang (Oak Ridge NL and Harvard)

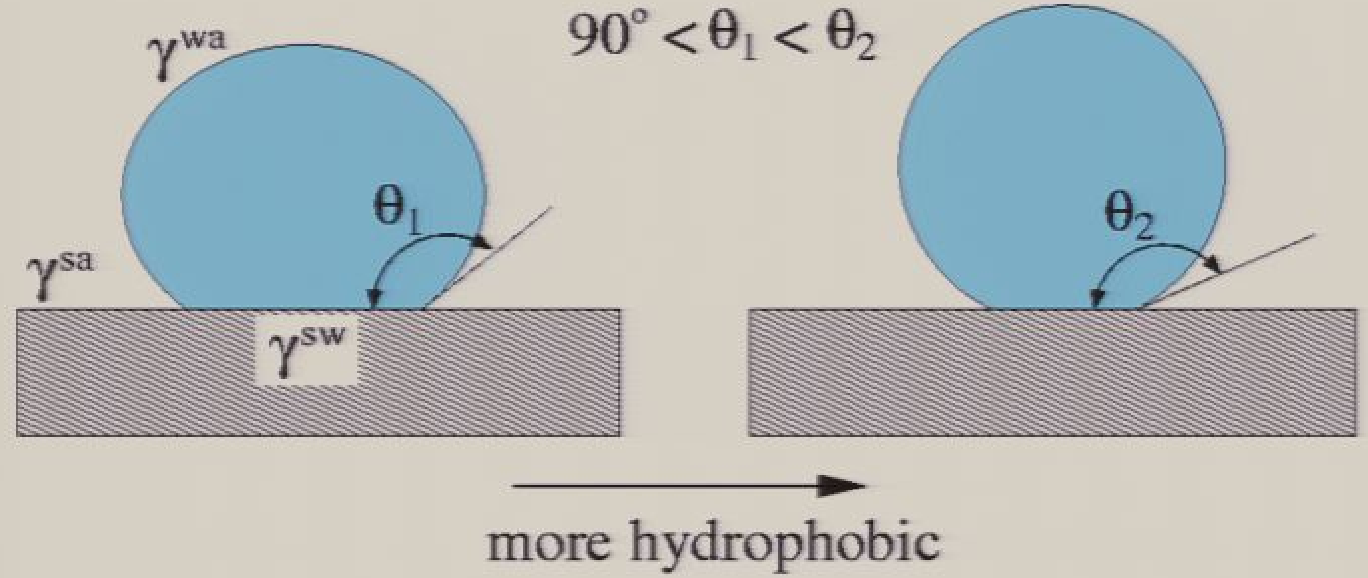


R. Langer and co-workers
Chemical & Biomedical Engineering, MIT

G. Whitesides and co-workers
Chemistry and Chemical Biology, Harvard

Polar head (hydrophilic)

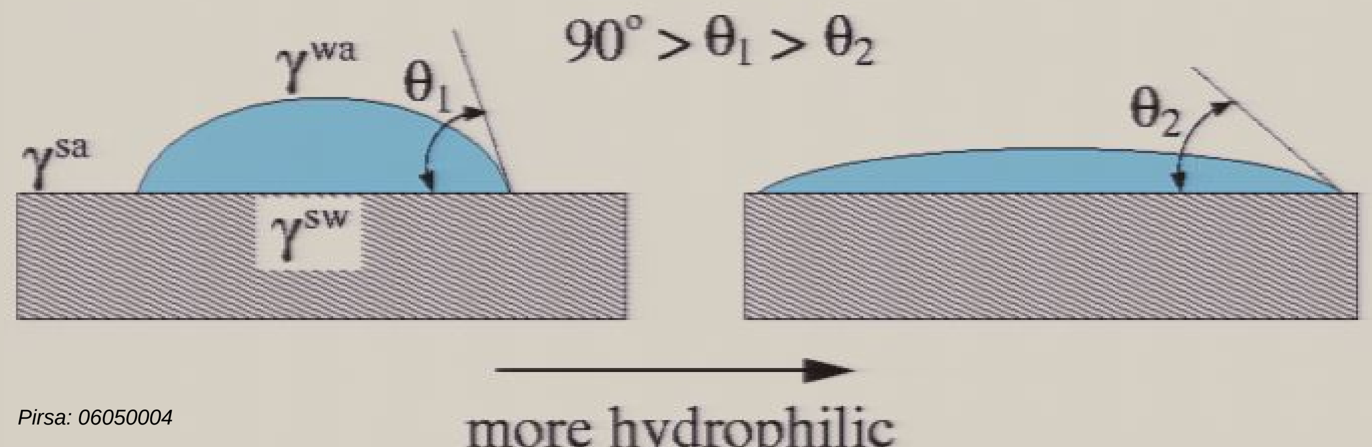
Non-polar chain (hydrophobic)



$\theta \rightarrow 180$:
super-hydrophobic

Young's equation
P.G. de Gennes,
Rev. Mod. Phys. **57** (1985)

$$\gamma^{sa} - \gamma^{sw} = \gamma^{wa} \cos(\theta)$$



$\theta \rightarrow 0$:
super-hydrophilic

iu, Feng,Zhai,Jiang & Zhu, *Langmuir* **20**, 5659 (2004), "*Reversible vettability of ZnO film between superhydrophobicity and superhydrophilicity*"

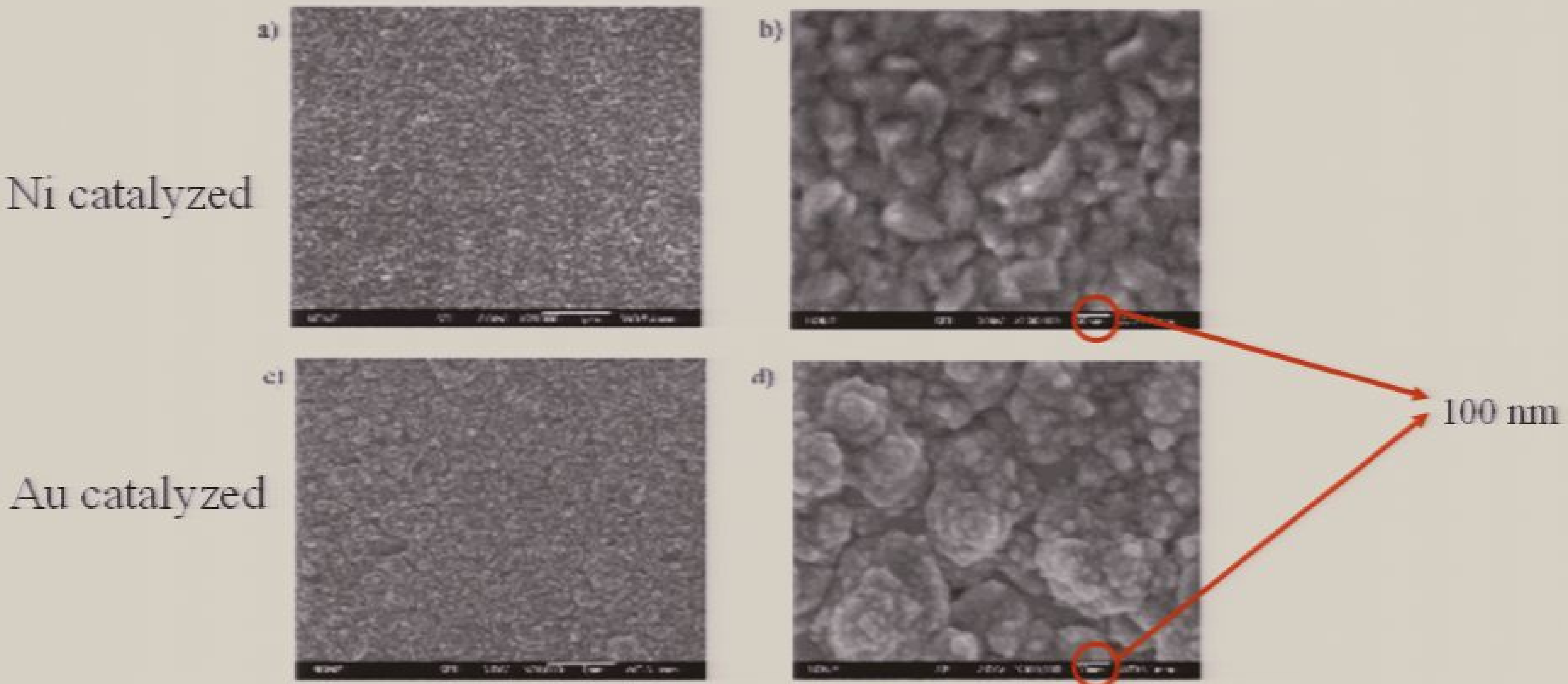
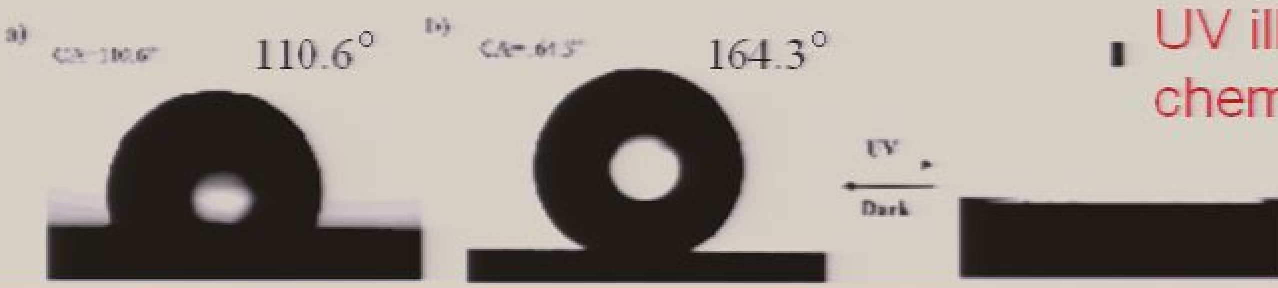


Figure 1. (a) Large-area SEM image of the film catalyzed by Ni; only submicrometer scale structures can be seen. (b) Enlarged view of part a. (c) Large-area SEM image of the superhydrophobic ZnO thin film, catalyzed by Au. (d) Enlarged view of several protuberances from part c, showing hierarchical structure.



- UV illumination = chemical modification

Figure 2. Shape of the water droplet on the corresponding surface described in Figure 1. (a) The water CA was 110.6° on the initial

W. Barthlott & C. Neinhuis

Planta **202**, 1-8 (1997)

"Purity of the sacred lotus,or escape from contamination in biological surfaces"

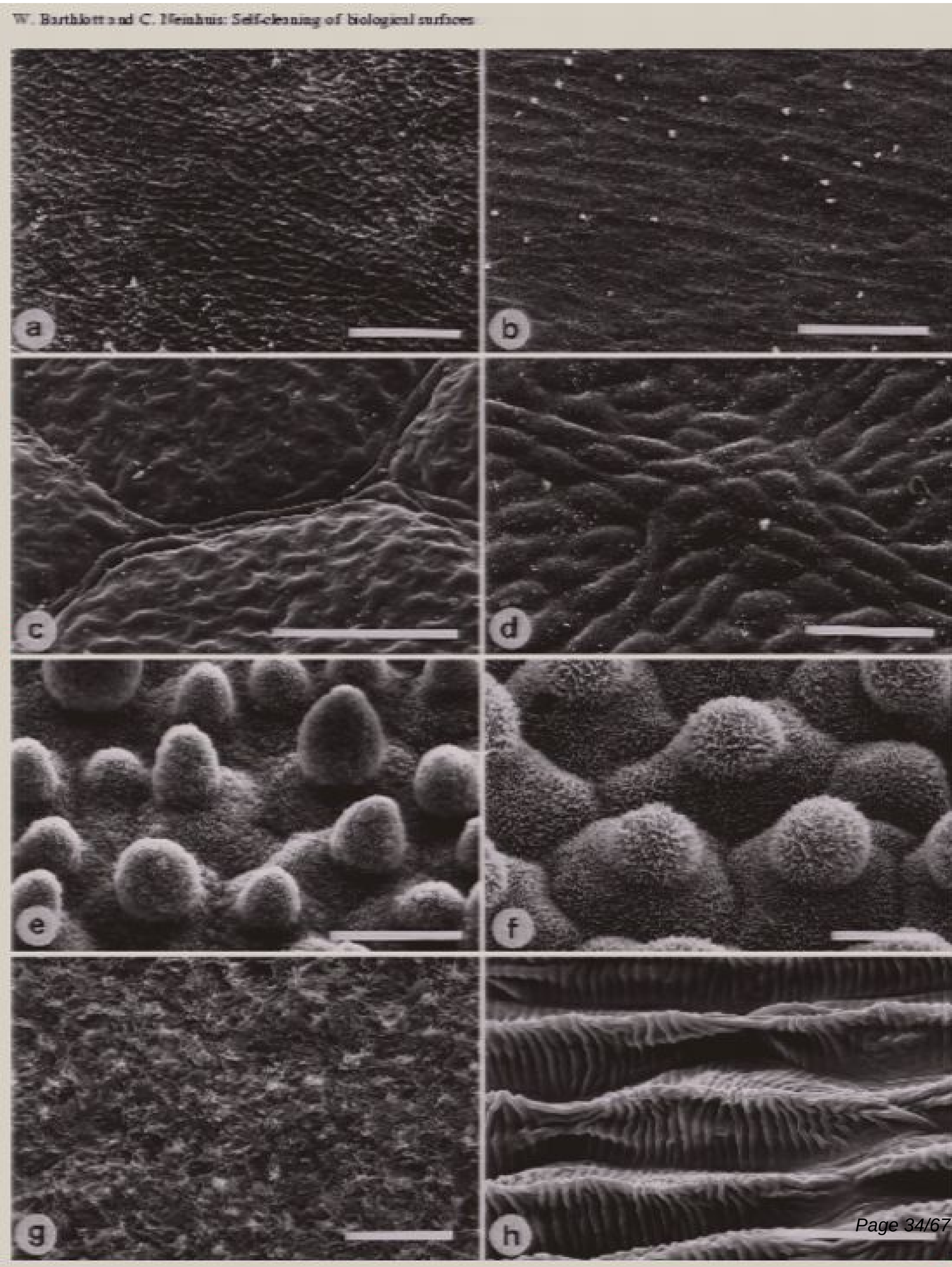
- a) *Gnetum gnemon*
- b) *Heliconia densiflora*
- c) *Fagus sylvatica*
- d) *Magnolia denundata*

wettable — 100 μ

- e) *Nelumbo nucifera*
- f) *Colocasia esculenta*
- g) *Brassica oleracea*
- h) *Mutisia decurens*

water repellent — 20 μ

"Lotus effect"



Superhydrophilic behavior - requirements:

1. Strong water molecule -surface interaction
   (but not too strong, no water dissociation)
2. Structural match between water (ice) – substrate
   diamond (wurtzite) lattice, no lattice strain
3. Biocompatibility

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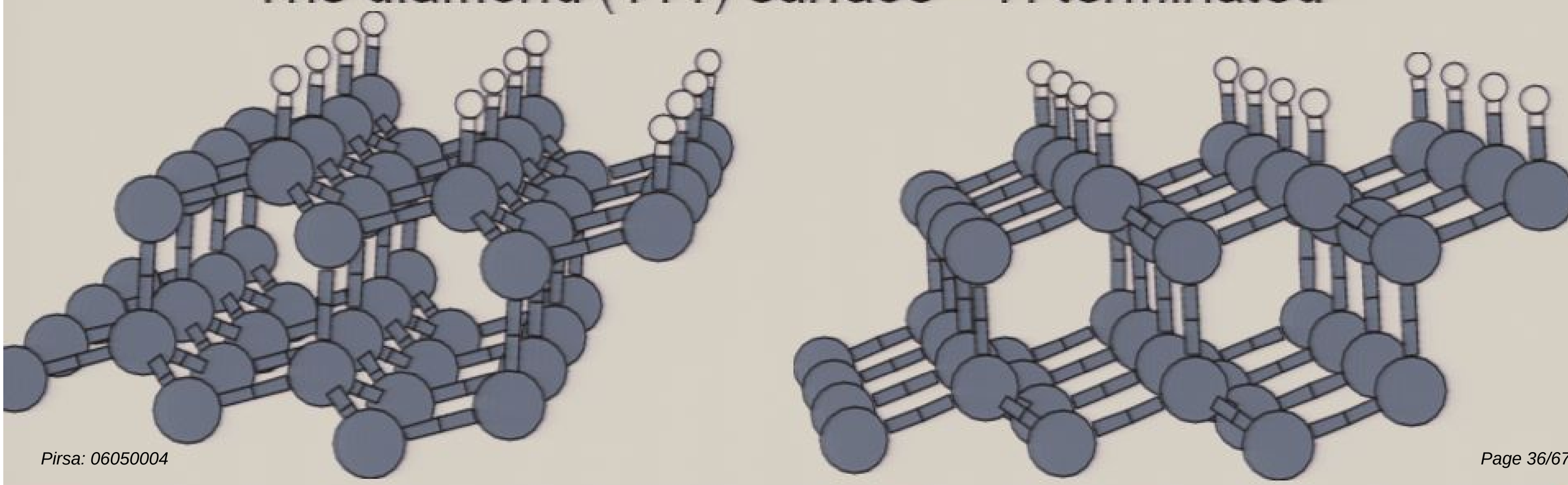
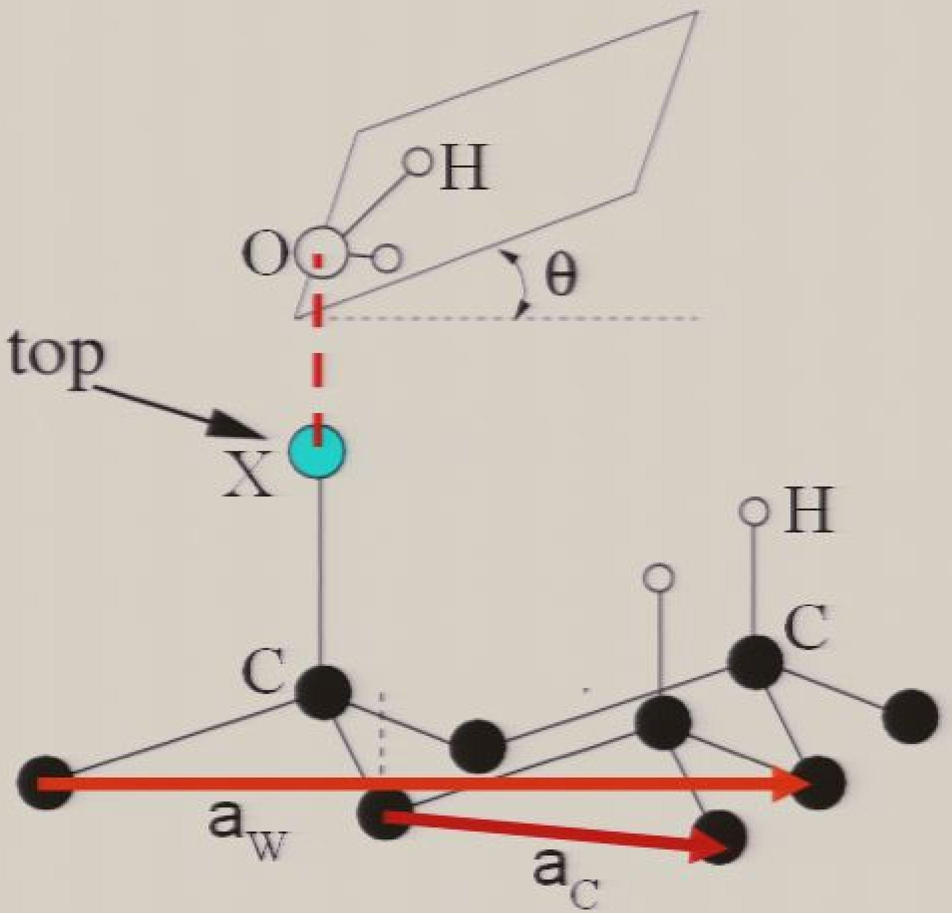
The diamond (111) surface – H terminated



Biocompatible, structural match with ice
(near-perfect lattice match, mismatch < 2%)



$$a_W = a_C (3)^{1/2}$$

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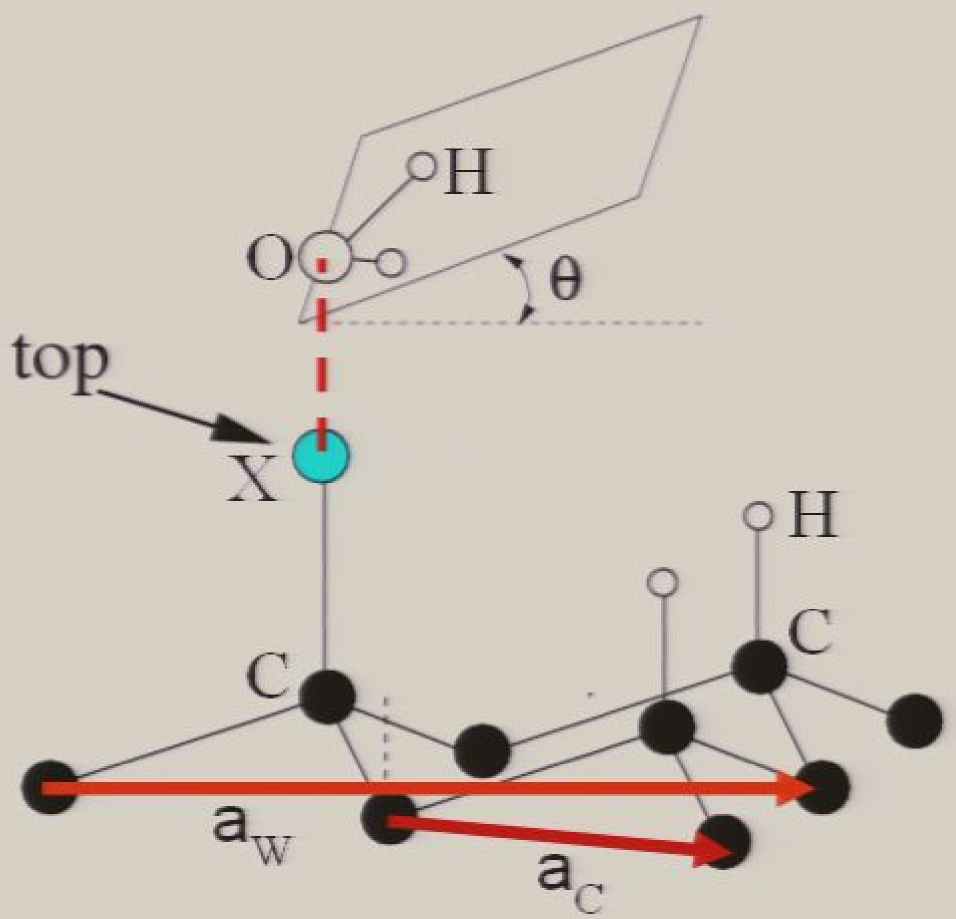
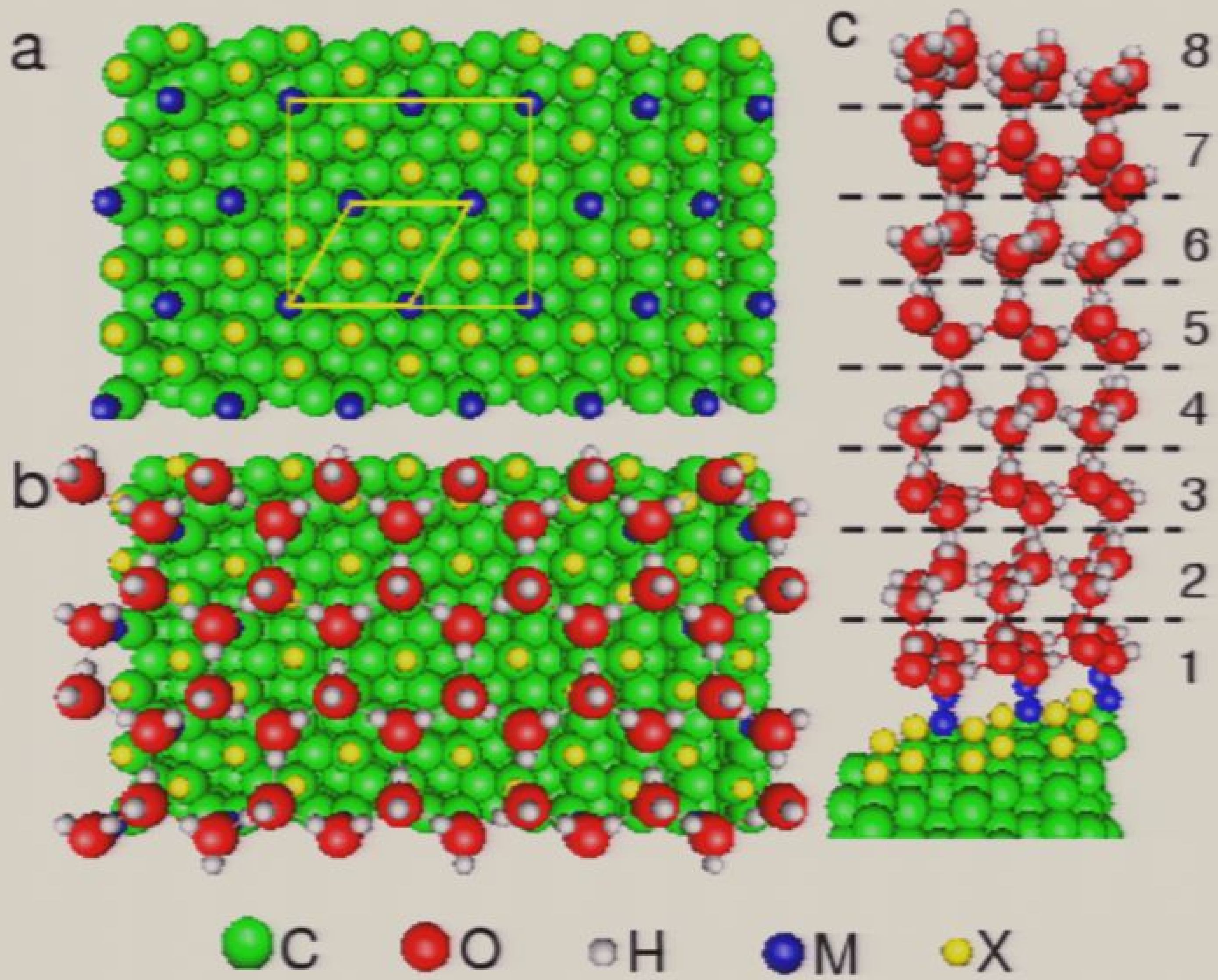


$a_W = a_C (3)^{1/2}$

Chemical modification of the H-terminated diamond (111) surface by submonolayer substitution?

Substitution of 1/3 monolayer of H by alkali metals

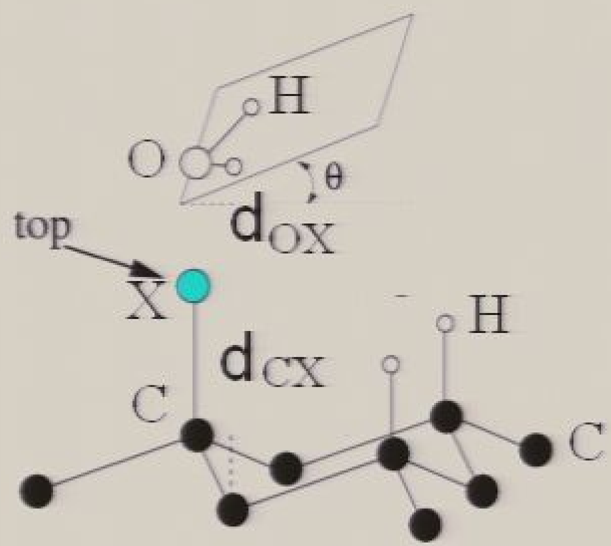


Structure and energetics of X-C(111)+water

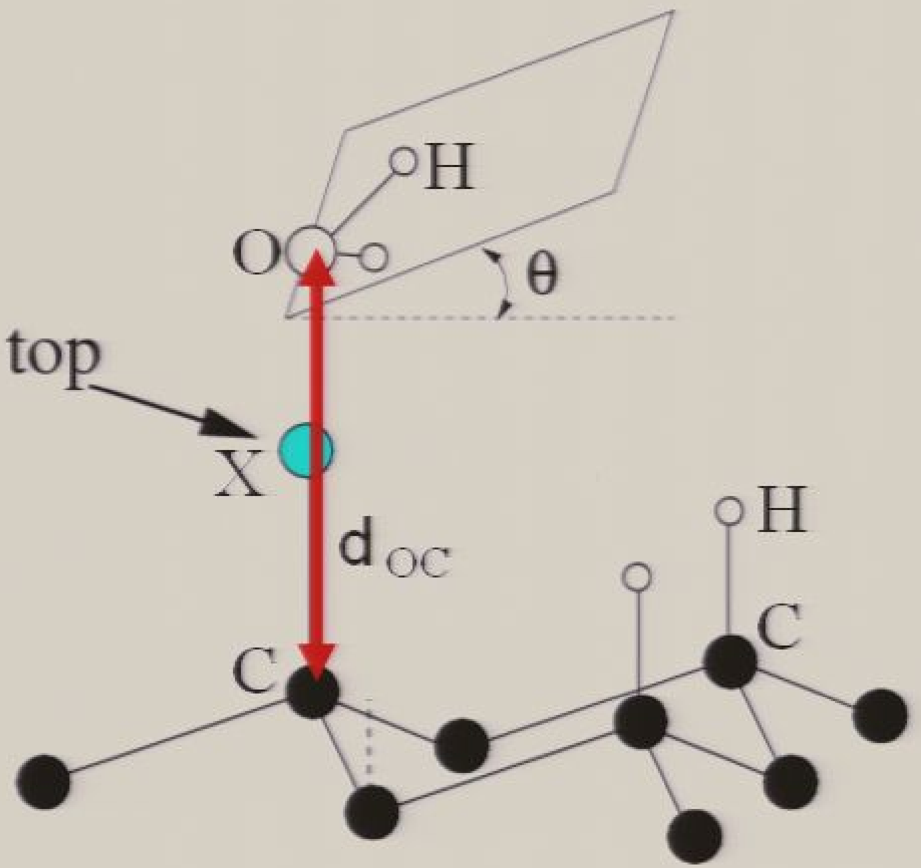
	H	Li	Na	K	F	Cl
d(CX)	1.11	2.14	2.50	2.85	1.44	1.85
d(OX)	2.58	1.95	2.38	2.70	2.04	2.66
θ	-2	37	40	40	90	90
E(molecule)	26	693	345	246	44	33
E(bilayer)	435	721	568	511	453	430

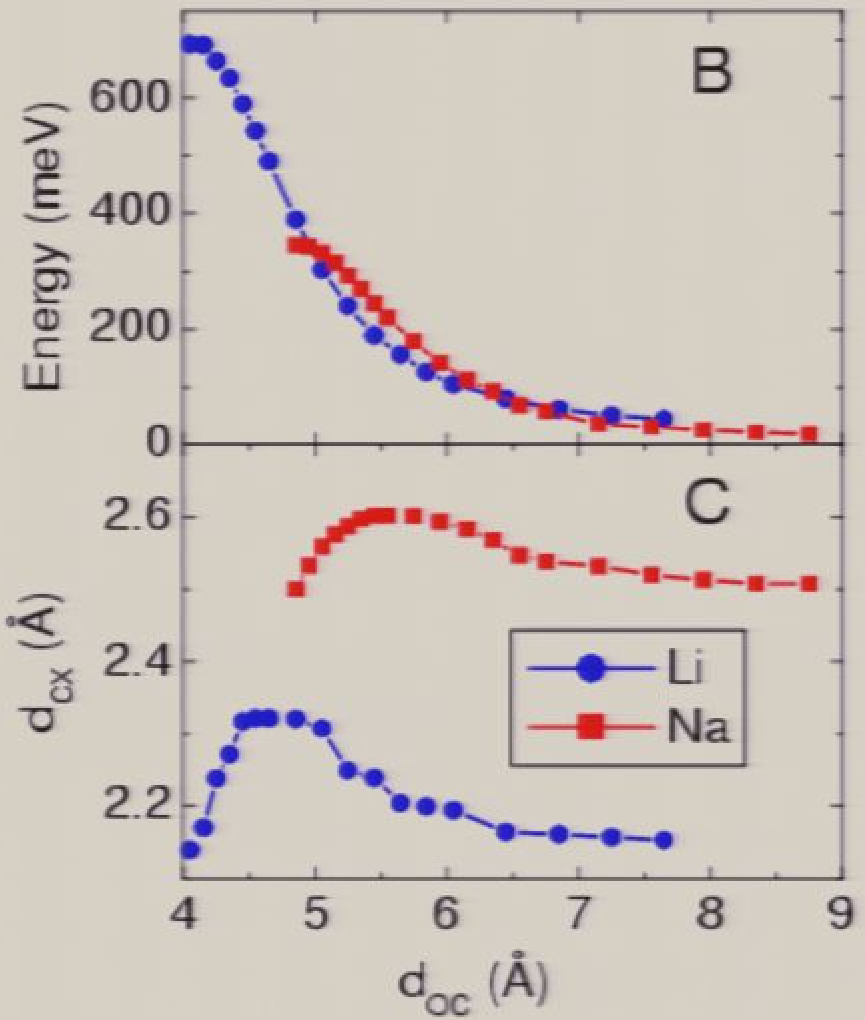
	Pt	Pd	Rh	Ru	MgO	Ice
E(bilayer)	534	546	562	660	601	**670**

Meng *et al.*, Phys. Rev. B (2004)
Feibelman, Science (2002)
Giordono *et al.*, PRL (1998)
Odelius *et al.* PRL (2004)



Stability of modified surface: water removal and chemical reactions





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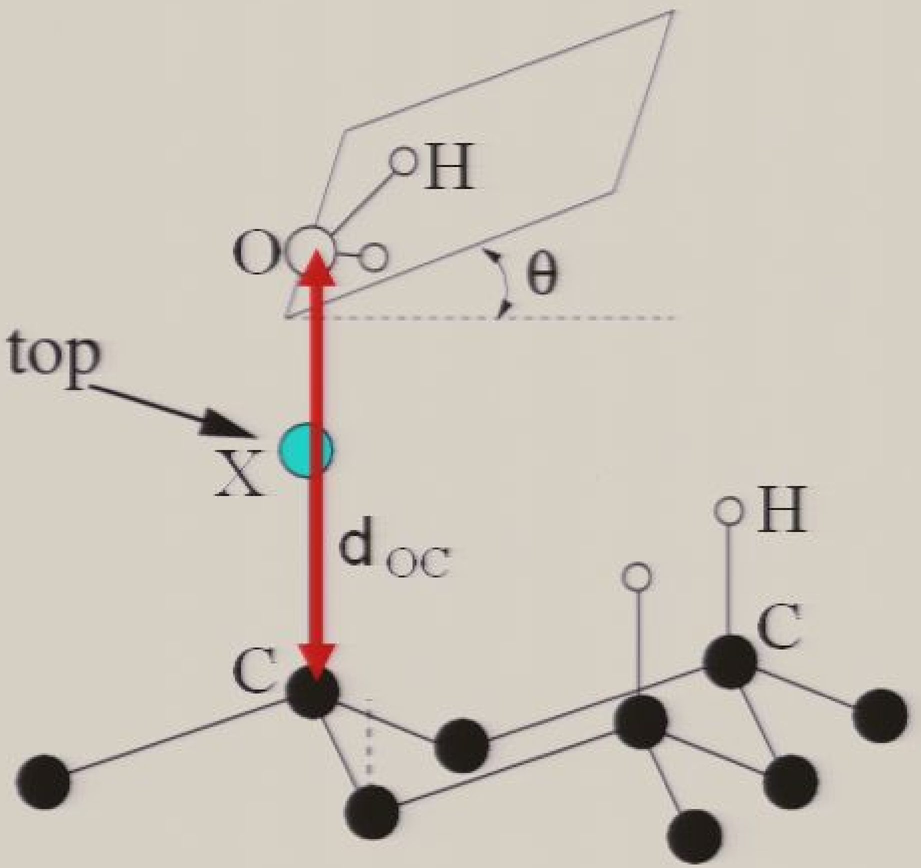
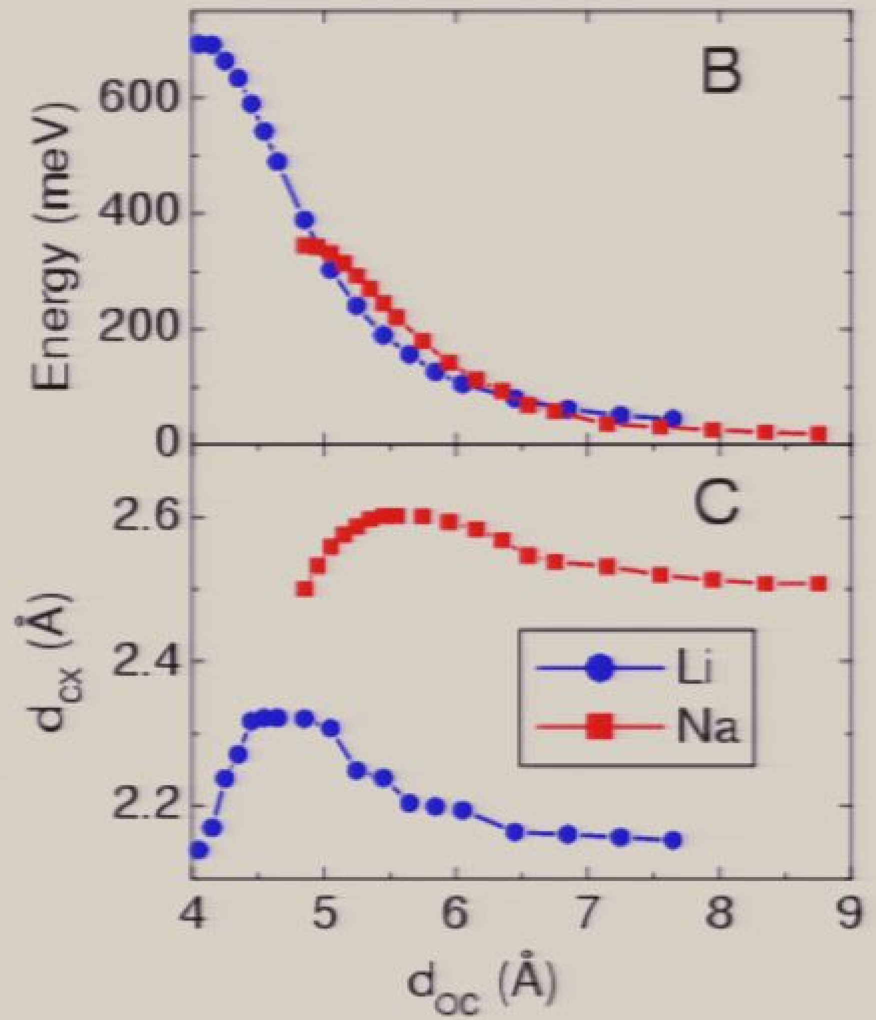
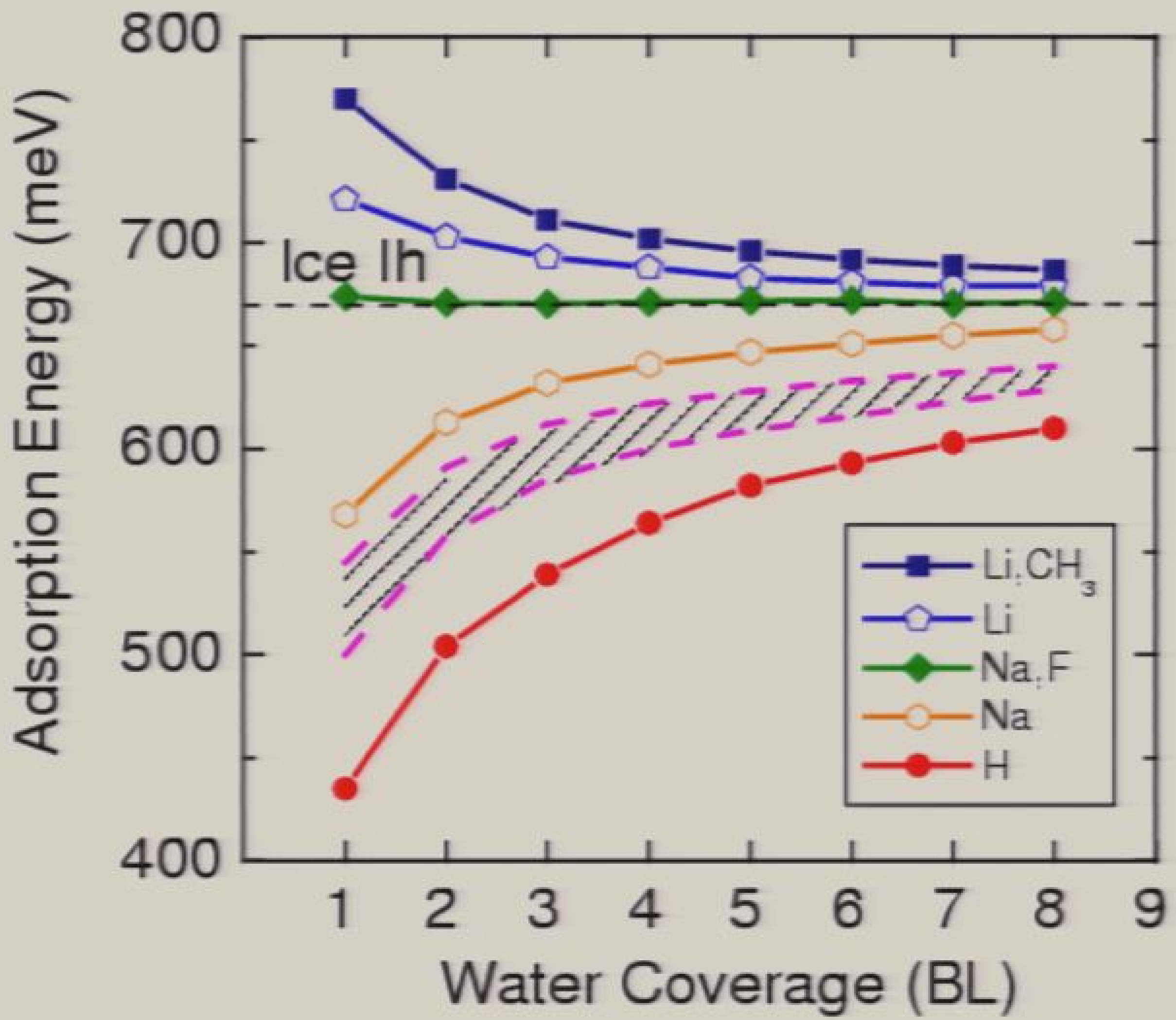
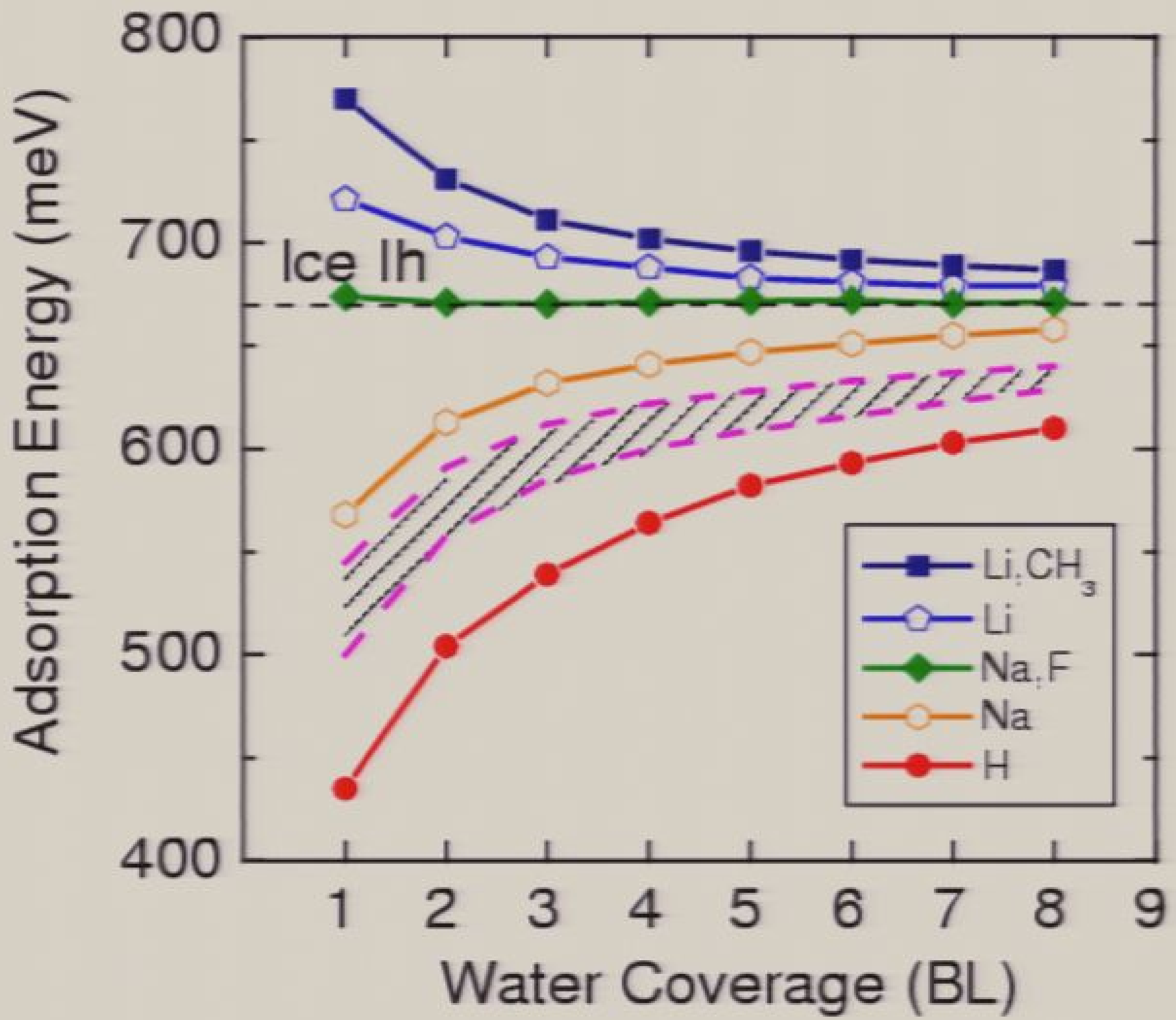




Li: unstable; Na: stable to reactions



800
700
600
500
400
Adsorption Energy (meV)
Ice Ih
1
2
3
4
5
6
7
8
9
Water Coverage (BL)
Li:CH3
Li
Na:F
Na
H



Ab-initio MD simulations (3 ps): stable at 310 K (body temperature)

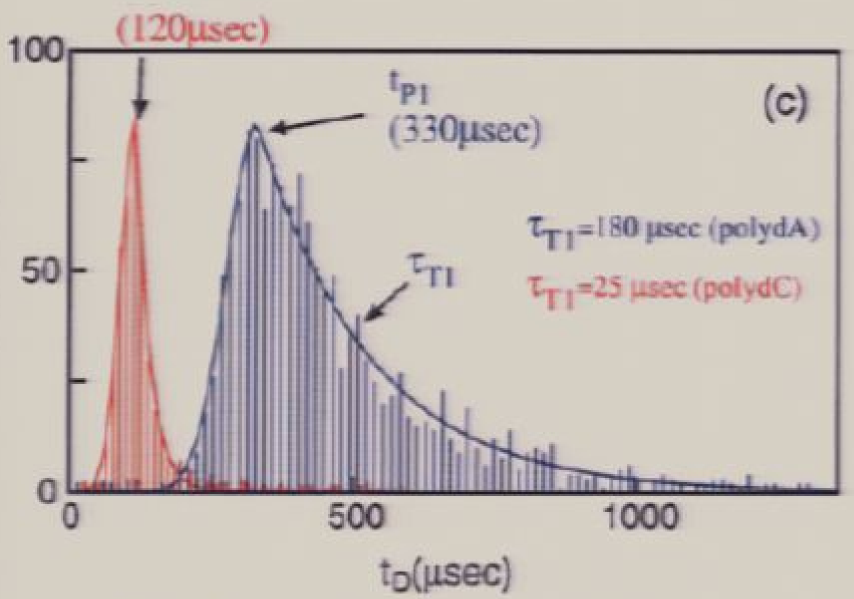
DNA translocation through nanopore

M. Fyta, S. Succi, S. Melchionna, E.K.

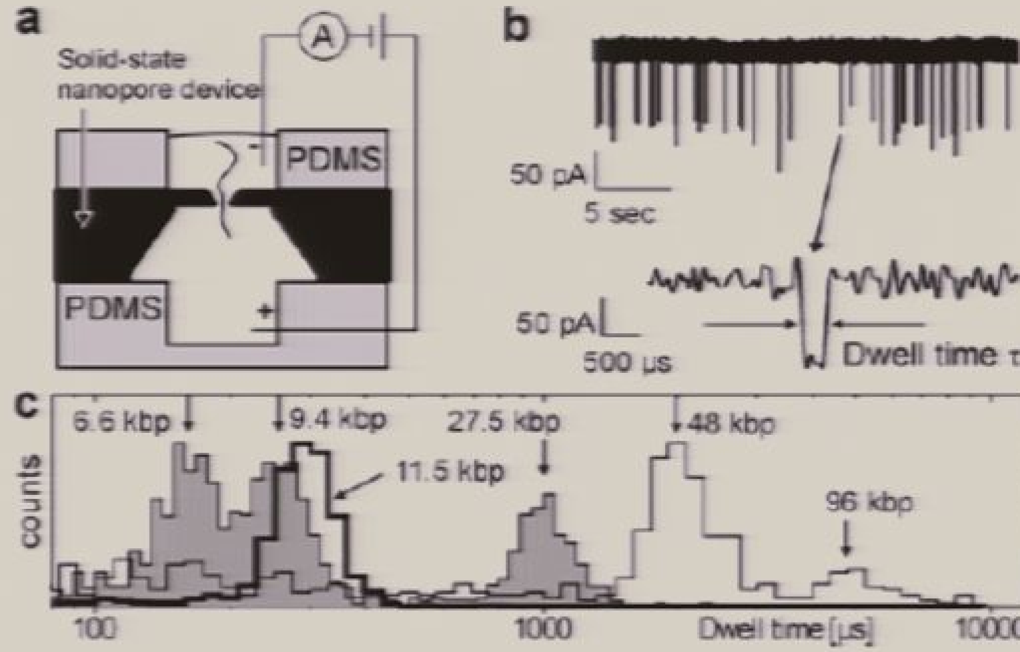
- Translocation of biopolymers (DNA, RNA, polypeptides) is important process in biology
  - viral injection of DNA into host cell or
  - passage of proteins through channels
- DNA penetration through narrow solid pores: ultrafast sequencing
- Previous Work:
  - Experiments: *In vitro* study of DNA translocation through nanopores by application of electric field in pore region
  - Theory: much analytical and simulational work, environment (solution) usually neglected

Double-stranded DNA (7 - 96 kbp)
passing through solid pore
forced by electric field at pore

Single-stranded DNA (100 bp)
passing through α-hemolysin
forced by ionic current



Meller et al., PNAS (2000)



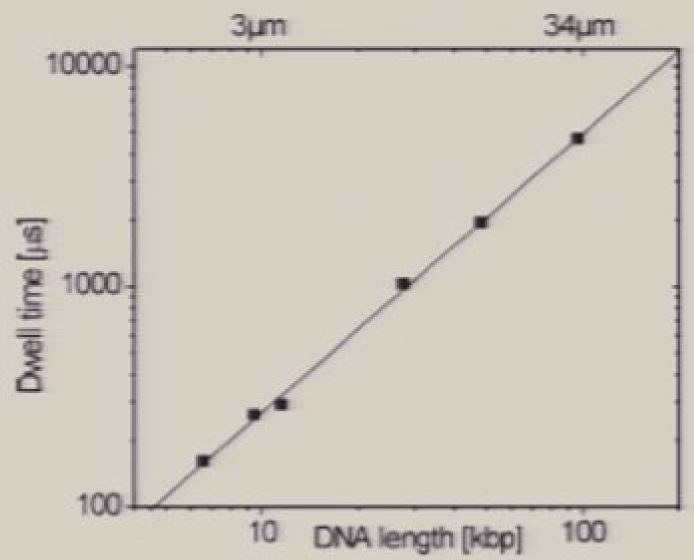


Figure 2. Dwell time versus DNA length. The line shows the result of a power-law fit to the data, with a best-fit exponent of $\alpha = 1.27 \pm 0.03$.

Storm et al., Nano Lett (2005)

Multiscale approach to DNA translocation

Force applied at the hole region to describe effect of electric field in experiments

– ***Molecular Dynamics*** for DNA

– ***Lattice Boltzmann Equation*** for the solvent

→ **Coupling of LBE to MD**

Lattice-Boltzmann Method (LB)

Lattice Boltzmann Equation for a set of discrete distribution functions:

$f_i(\mathbf{x},t)$, i=1,n: probability to find a particle at lattice site **x** at time t with speed $\mathbf{c_i}$

$$f_i(\vec{x} + \vec{c}_i \Delta t, t + \Delta t) = f_i(\vec{x},t) + \omega \Delta t (f_i - f_i^{eq})(\vec{x},t) + S_i \Delta t$$

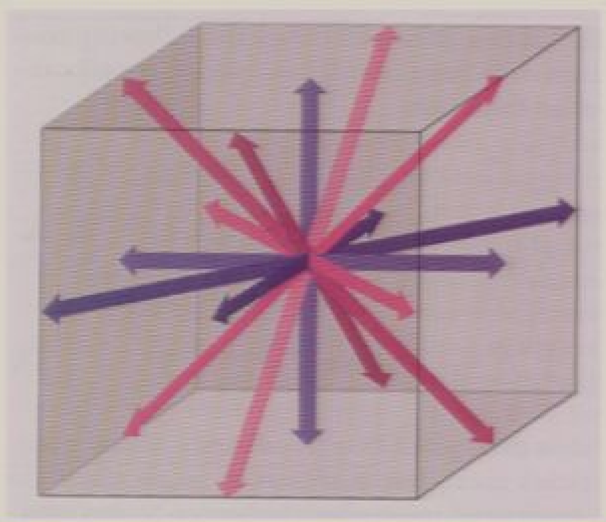
polymer-fluid back reaction

local equilibrium : $$f_i^{eq} = w_i[\beta \vec{u} \bullet \vec{c}_i + \frac{\beta}{2}(\vec{u}\vec{u} \bullet (\vec{c}_i \vec{c}_i - \frac{1}{\beta} I))]$$

$\beta = 1/kT$

Fluid particles move only along trajectories prescribed by the lattice directions

(in 3D: 19-speed lattice)



Molecular (Langevin) Dynamics (MD)

DNA with N beads at positions $\mathbf{r_p}$ with velocities $\mathbf{u_p}$:

$$\frac{d\vec{r}}{dt} = \vec{u}_p$$

$$m\frac{d\vec{u}_p}{dt} = \vec{F}_p^c + \vec{F}_p^f + \vec{F}_p^r + \lambda \partial_{\bar{r}_p} \sigma, \quad p = 1, N$$

bead-bead interactions

Solute-solvent interactions

random force

reaction force

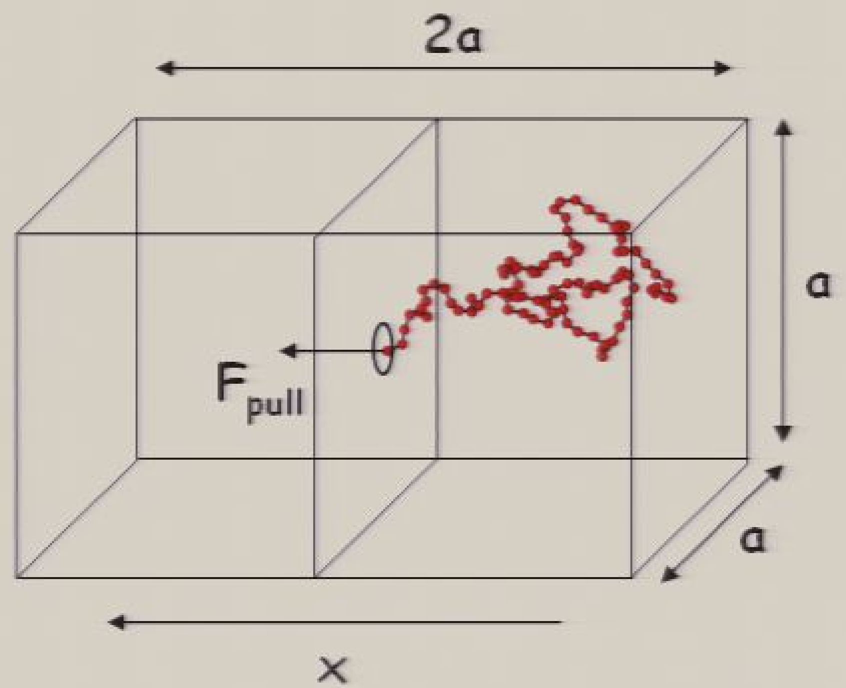
$\sigma \equiv \left| \bar{r}_{p+1} - \bar{r}_p \right|^2 - r_0^2 = 0$, r_0 bond length

Coupling LB to MD: $\vec{F}_p^f = \gamma(\vec{u}_p - \vec{U}_p)$

u bead velocity
U fluid velocity

Details of simulation

- 3D box of (2a x a x a) size
- hole size = 40 nm
- lattice spacing Δx = 20 nm



- F_{pull}=0.01, kT=10^{-5}
- Fast translocation regime :

$$\frac{F_{pull}R}{kT} >> 50$$

[translocation time << DNA relaxation time]

Solvent : ρ=1 (density)
γ=0.1 (damping coefficient)
ν=0.1 (kinematic viscosity)

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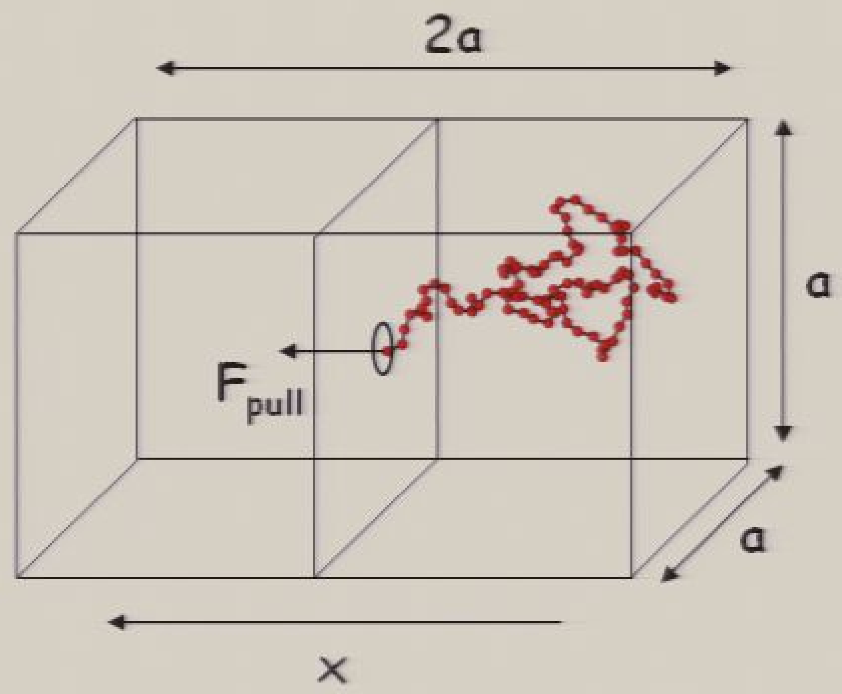

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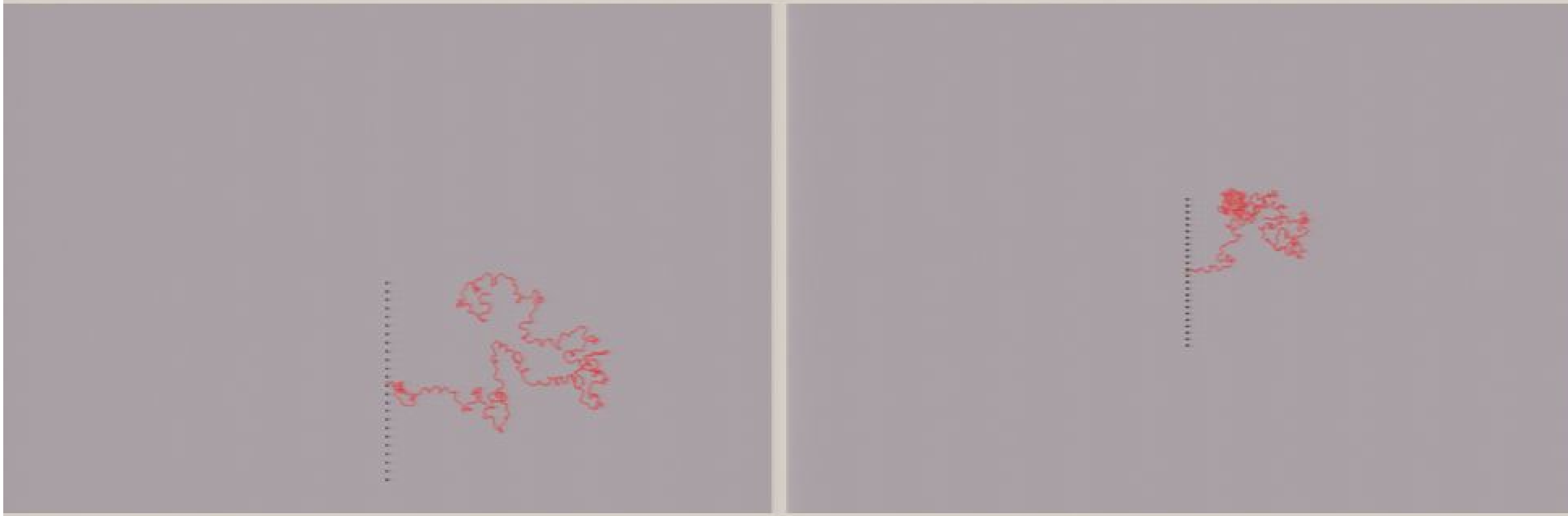
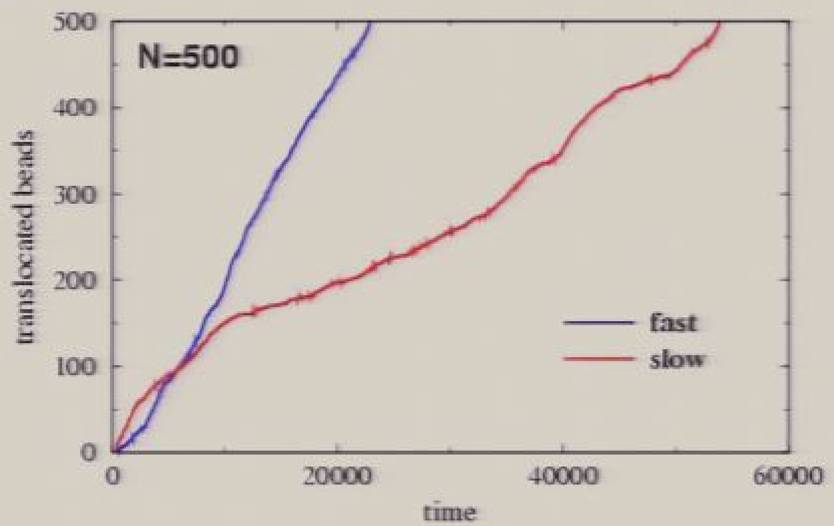
[translocation time << DNA relaxation time]

Solvent : ρ=1 (density)
γ=0.1 (damping coefficient)
ν=0.1 (kinematic viscosity)

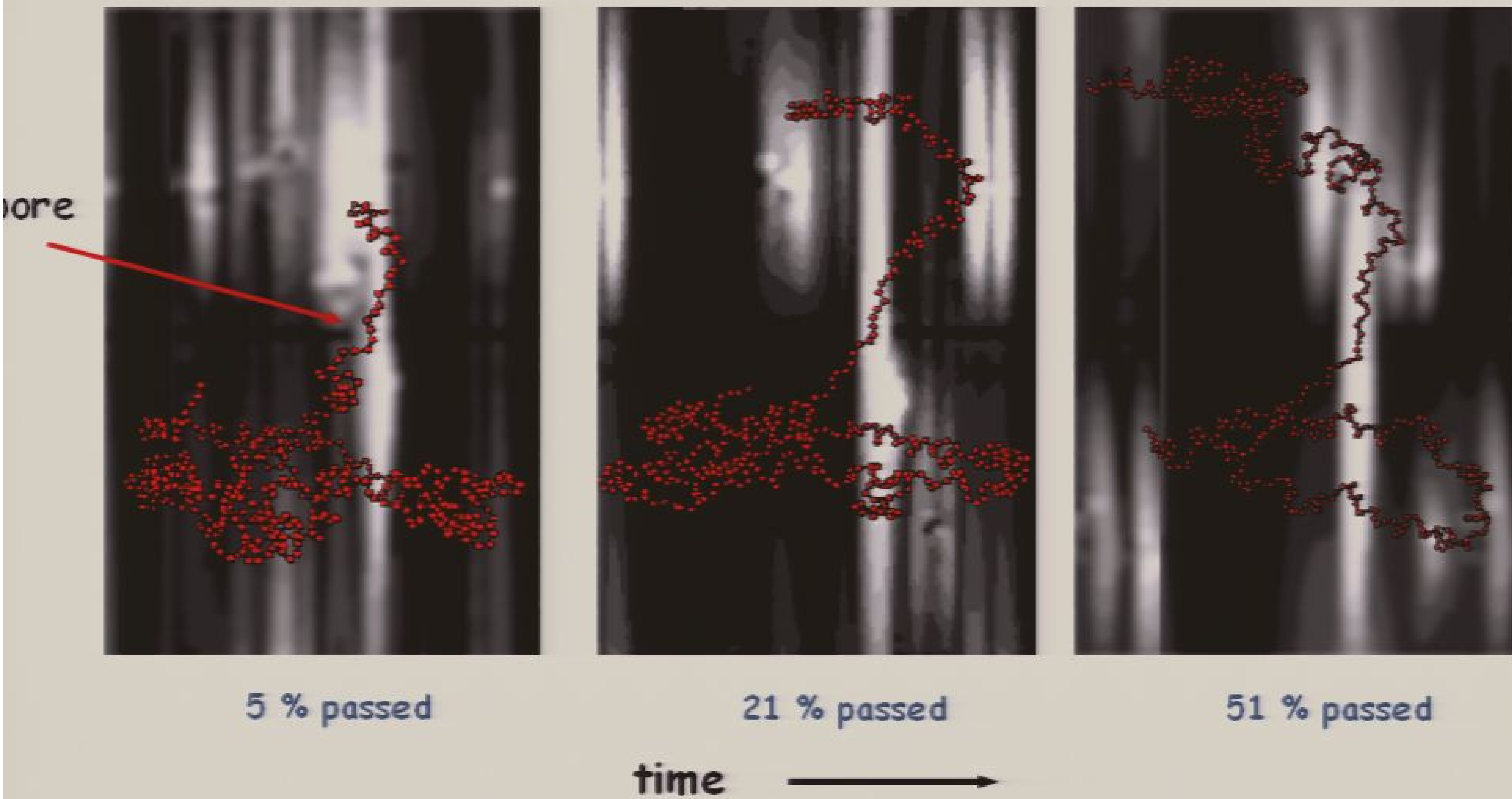
DNA beads : 20 ≤ N ≤ 700
1 bead ~ 10 - 100 bp

Fast vs. Slow Translocation



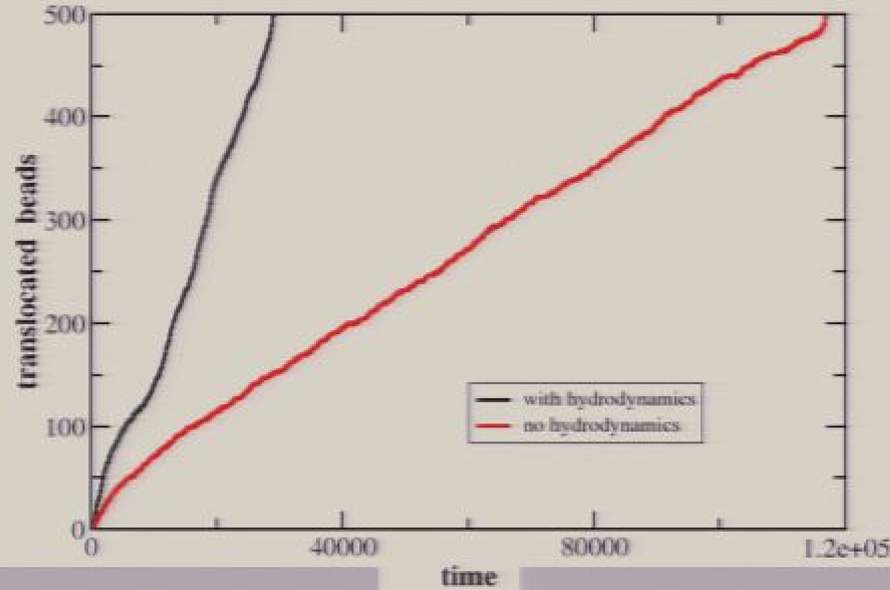


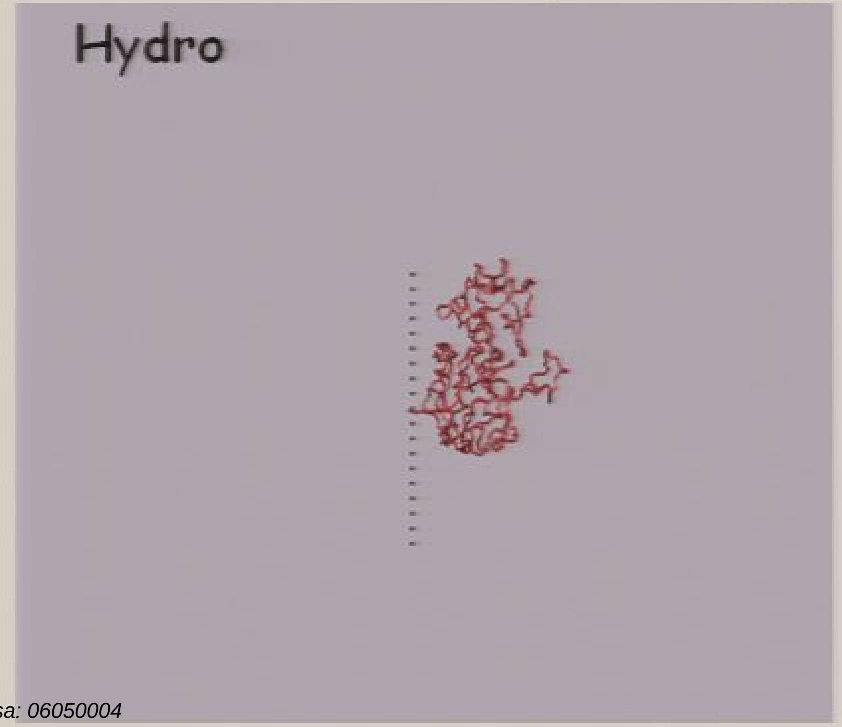
Fluid motion:
black: zero velocity, white: high velocity

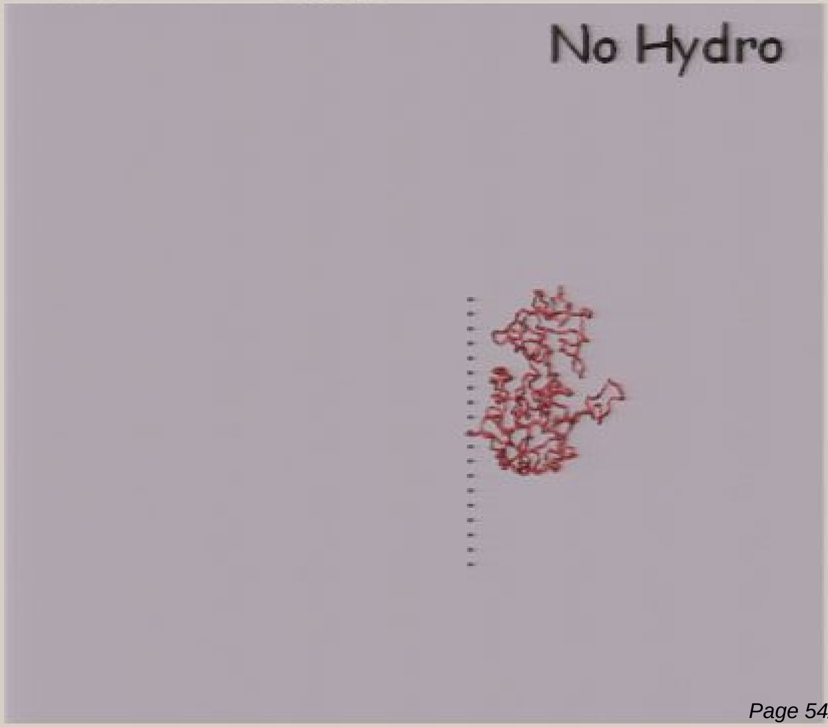


Hydro vs. No Hydro

N=500







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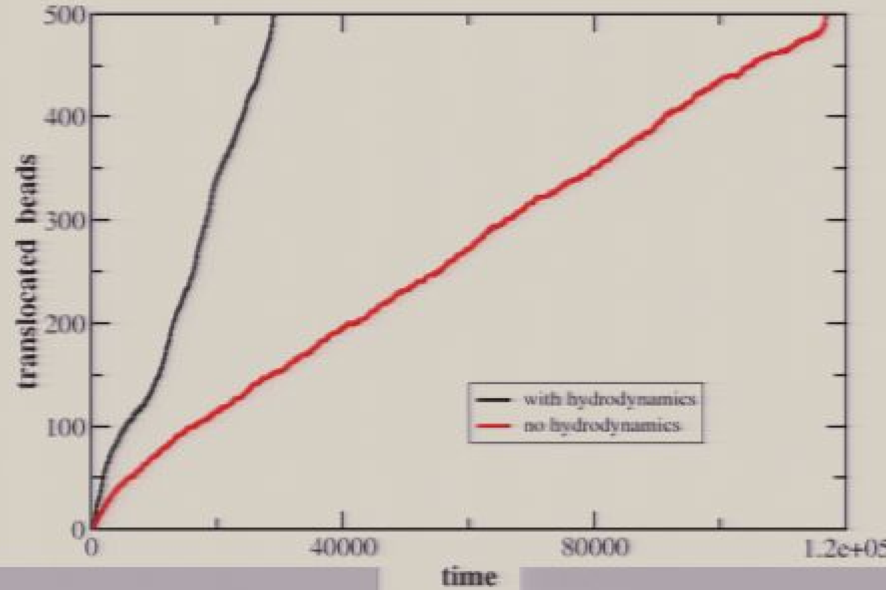

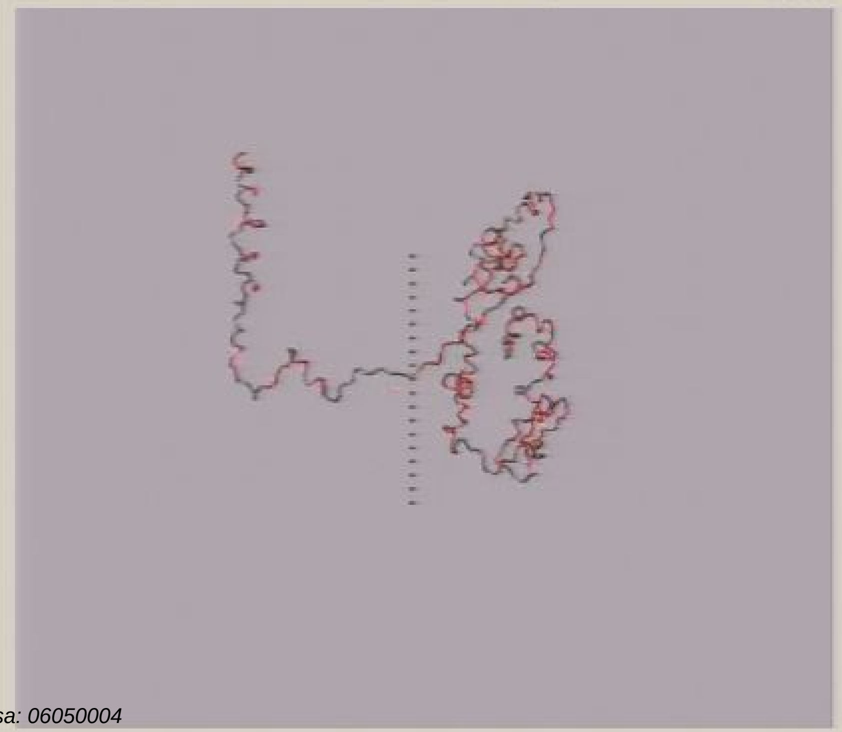

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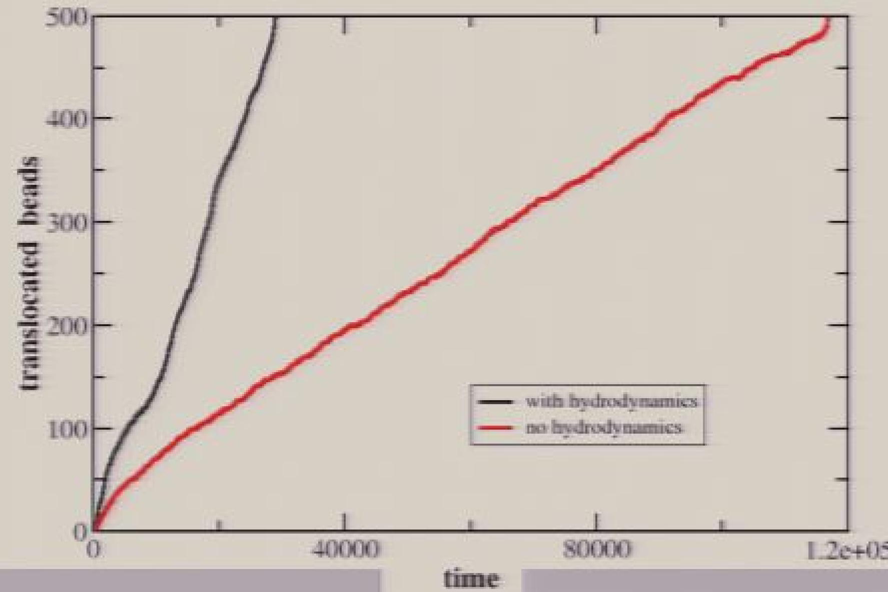

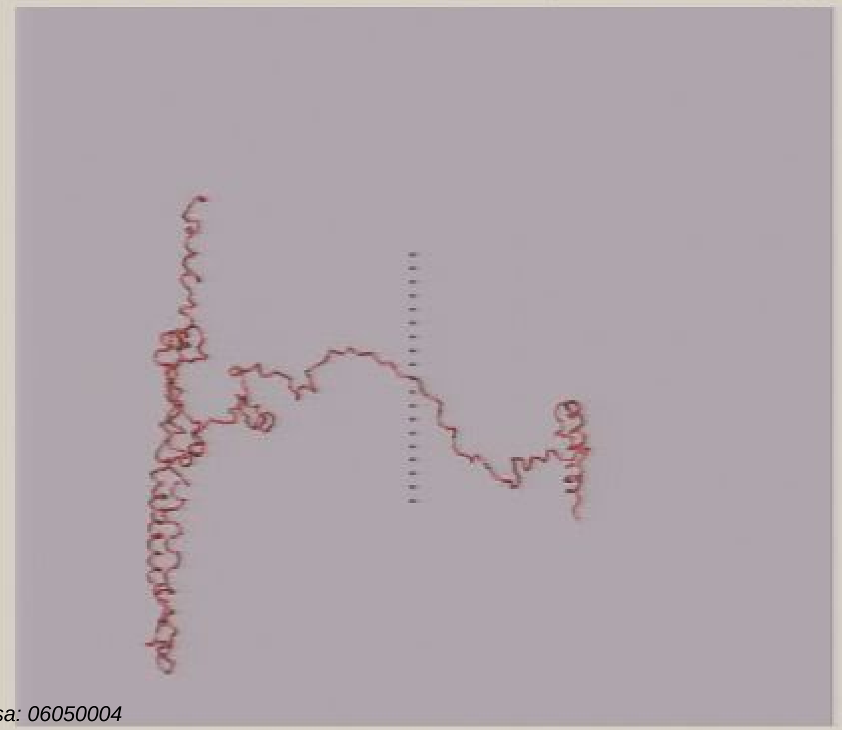

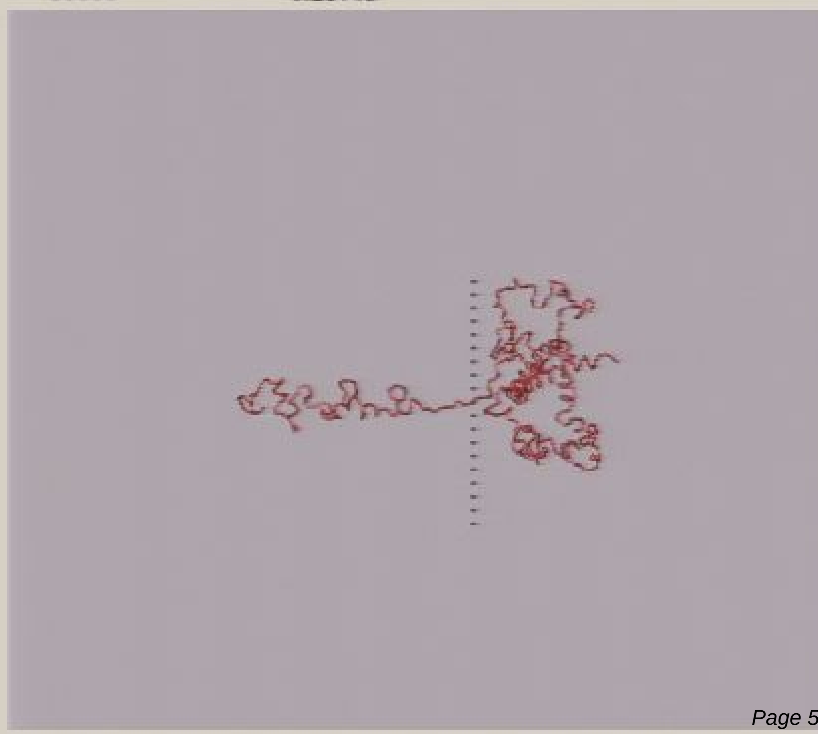

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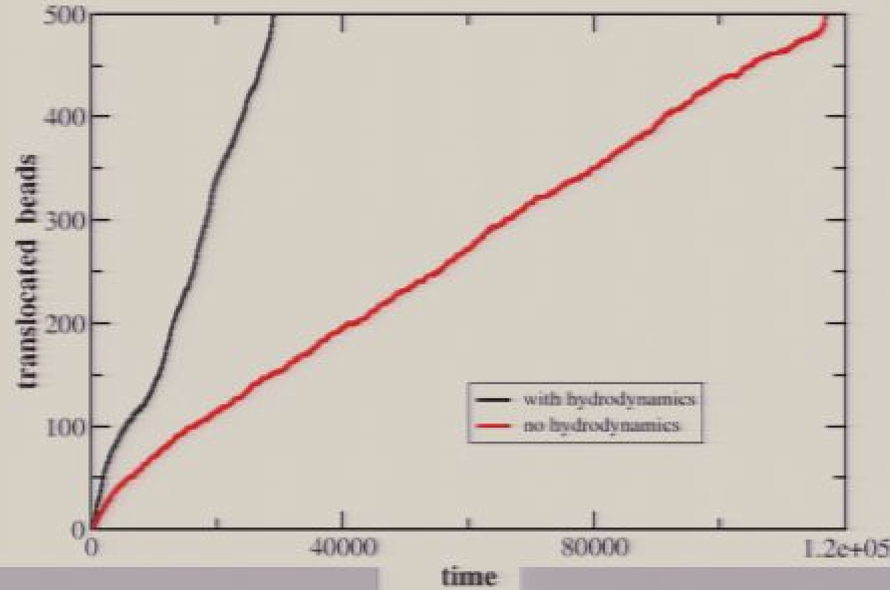

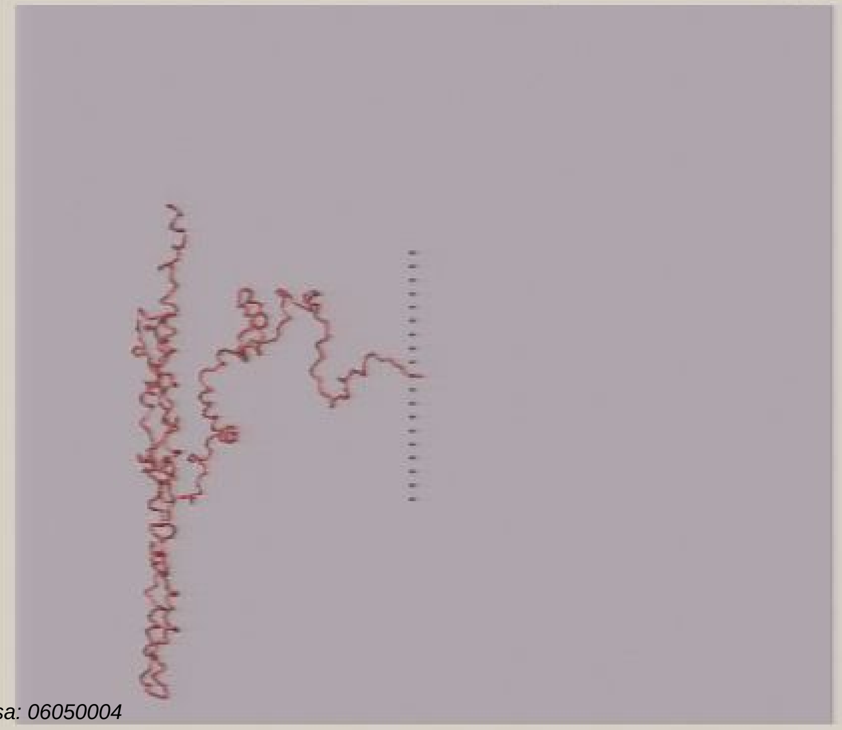

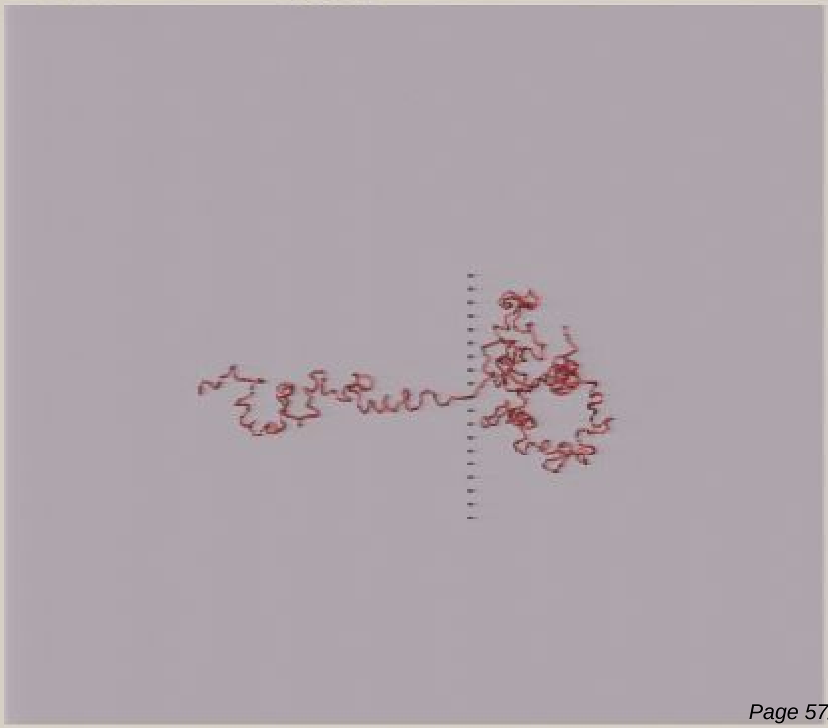

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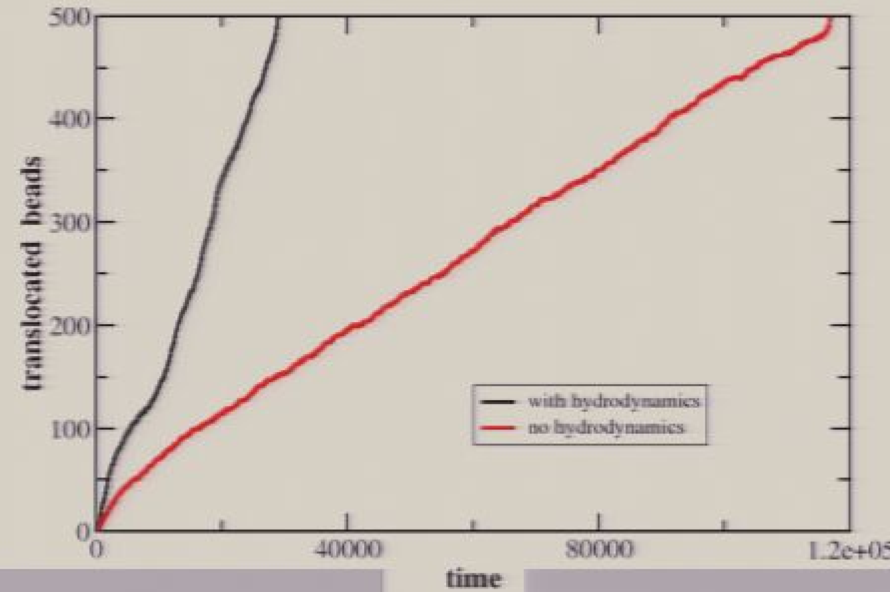

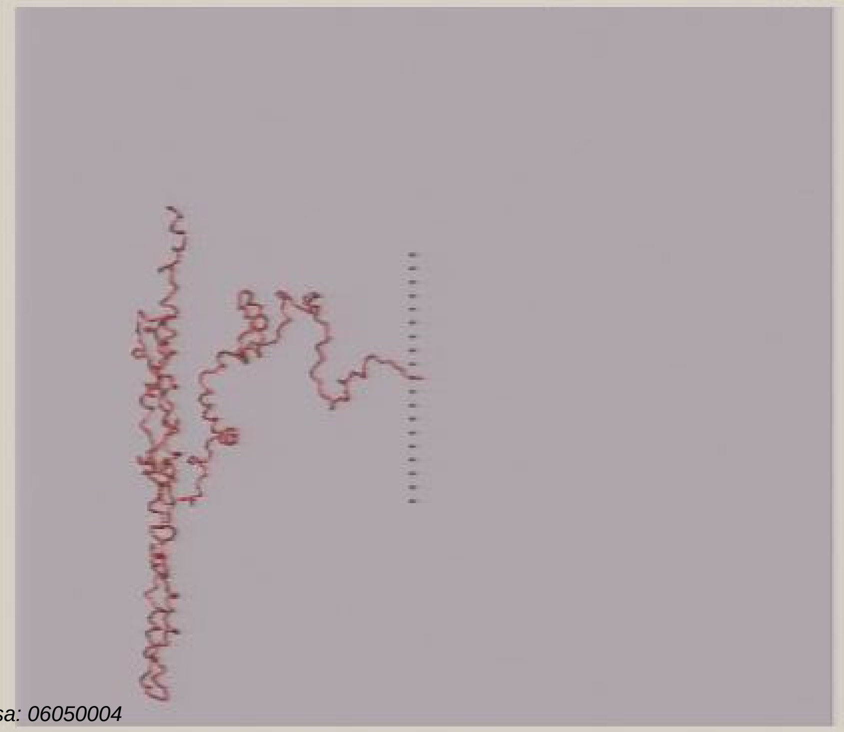

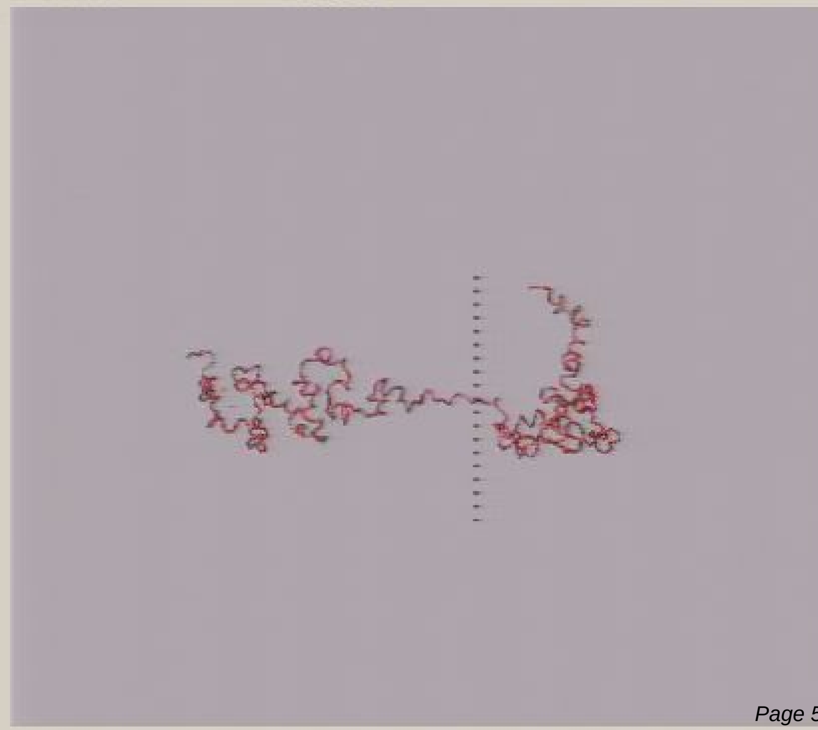

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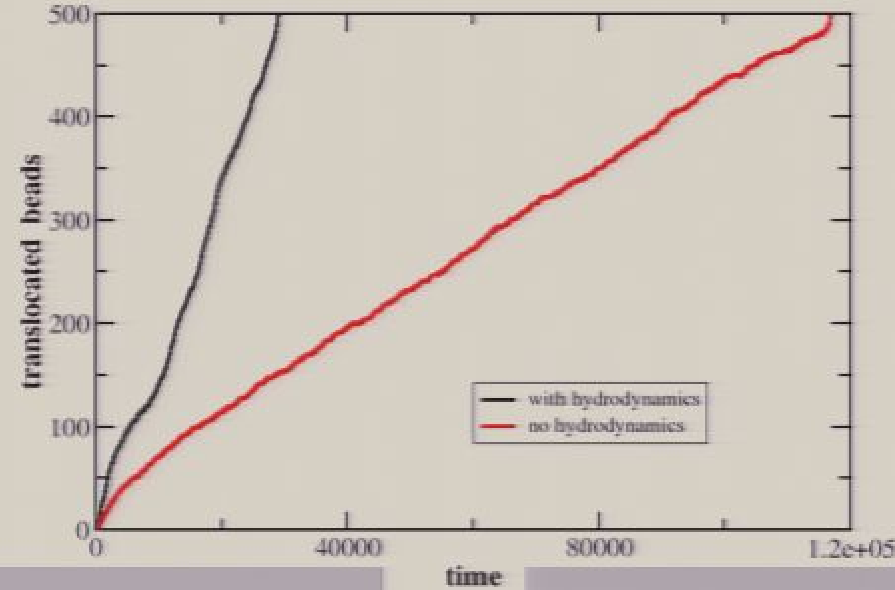

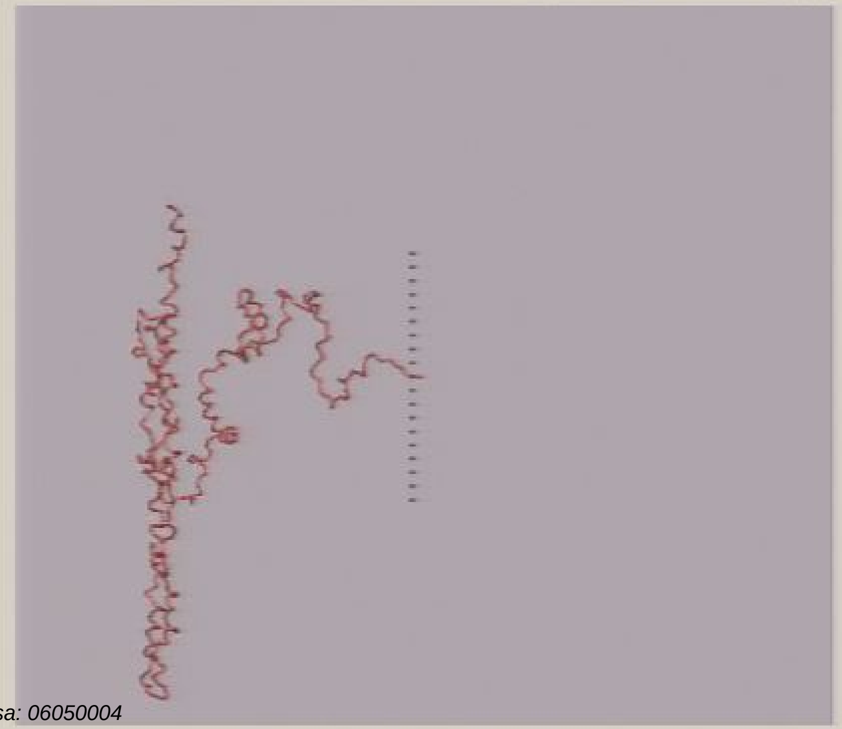

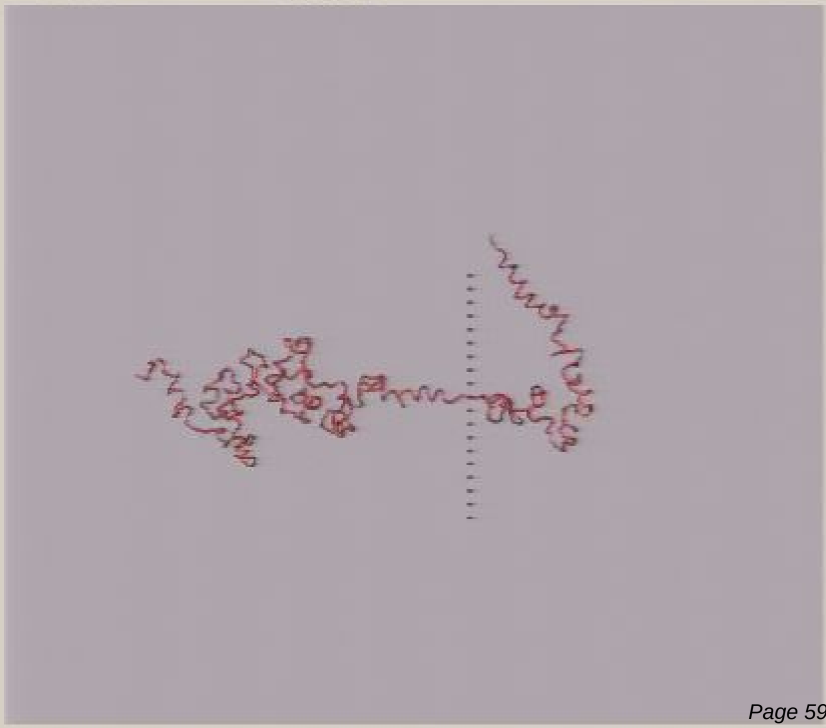

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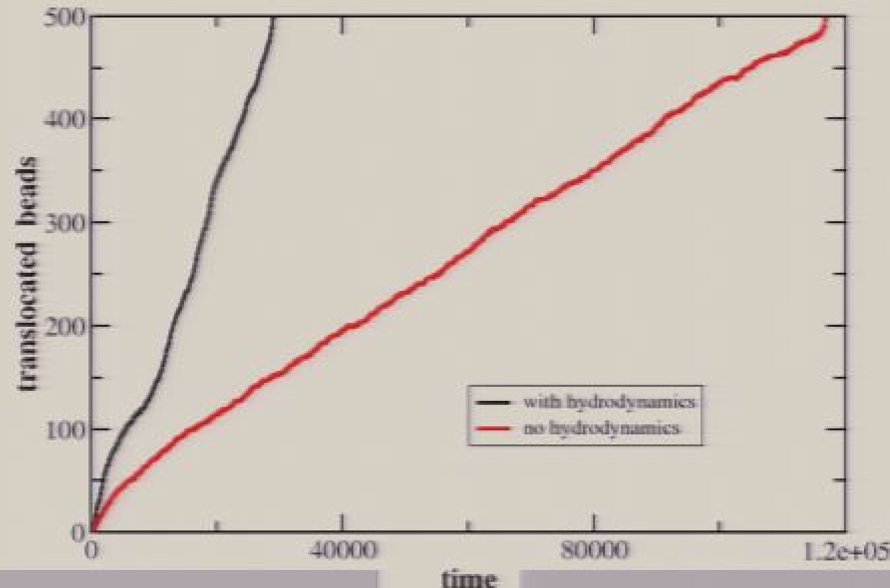

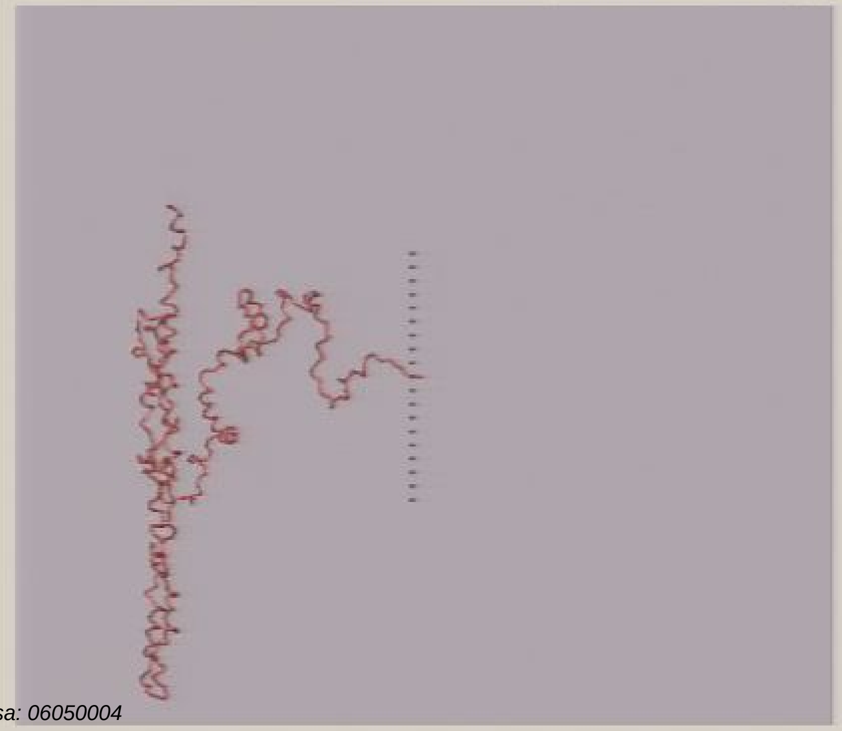

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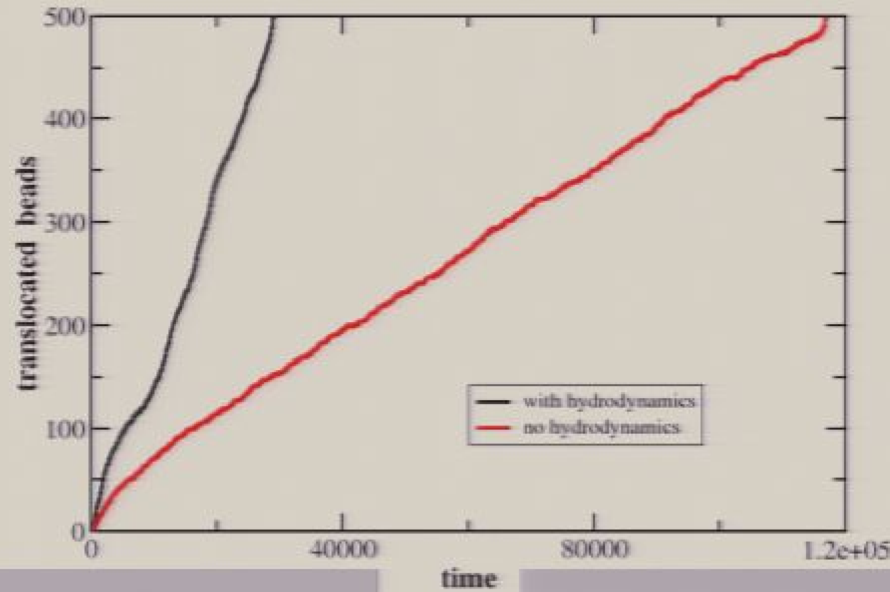

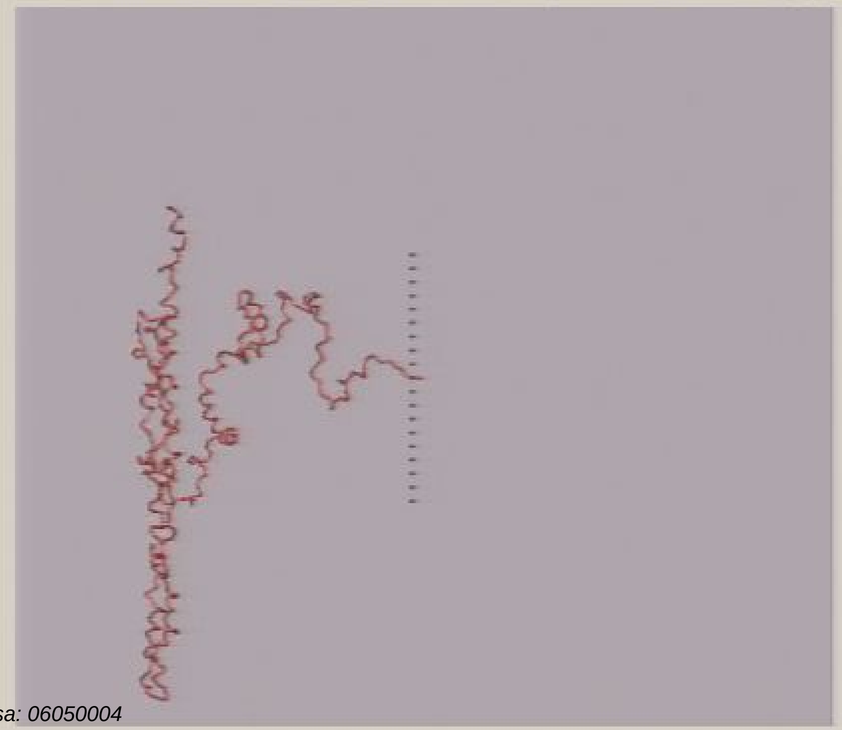

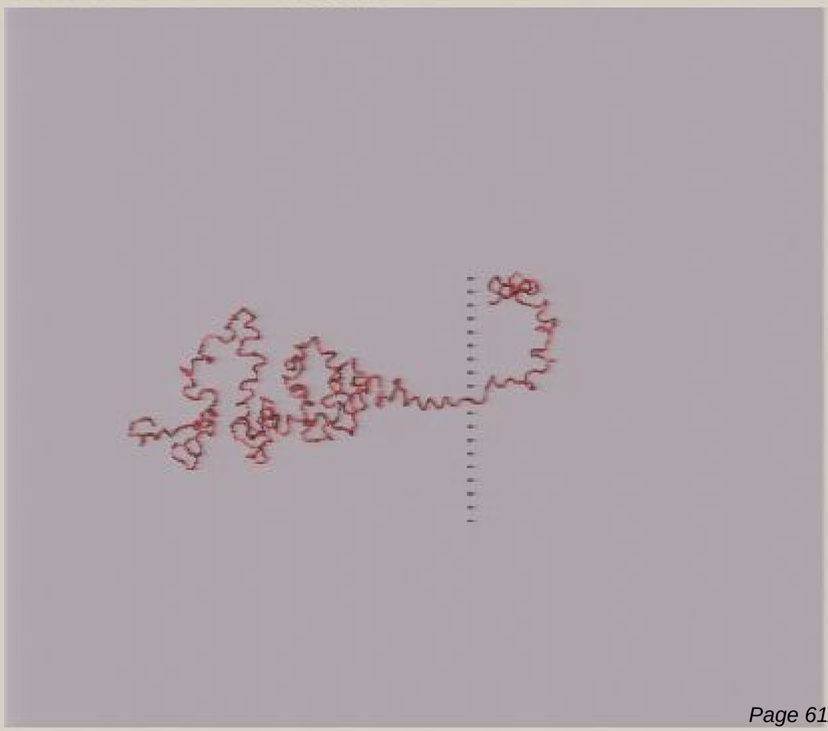

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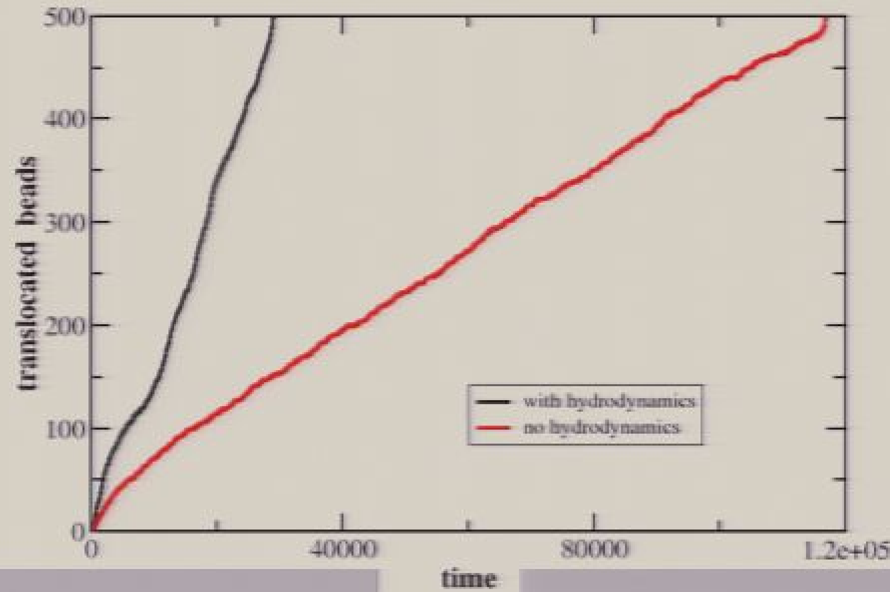

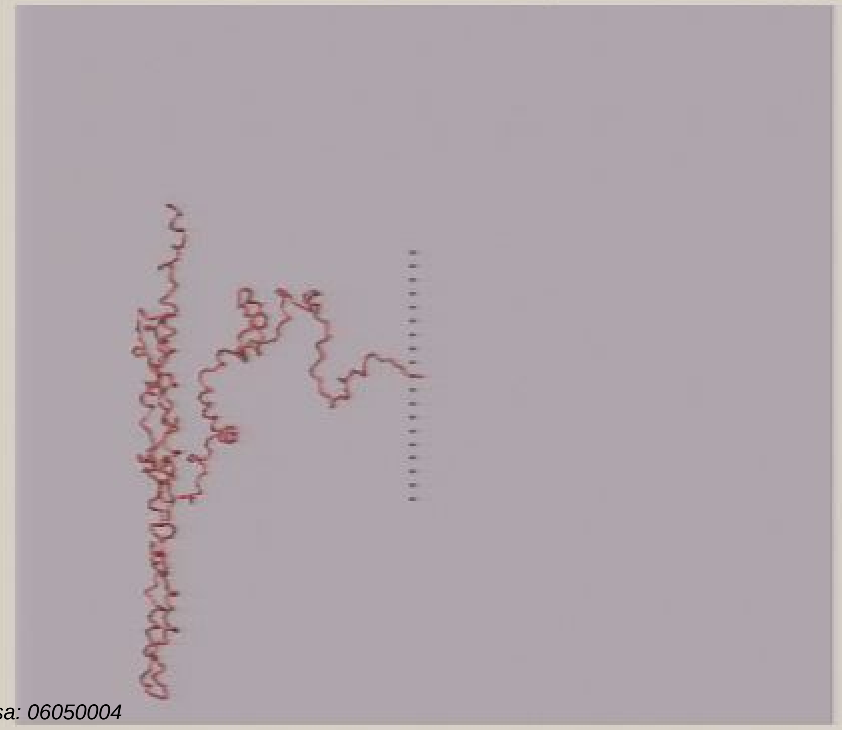

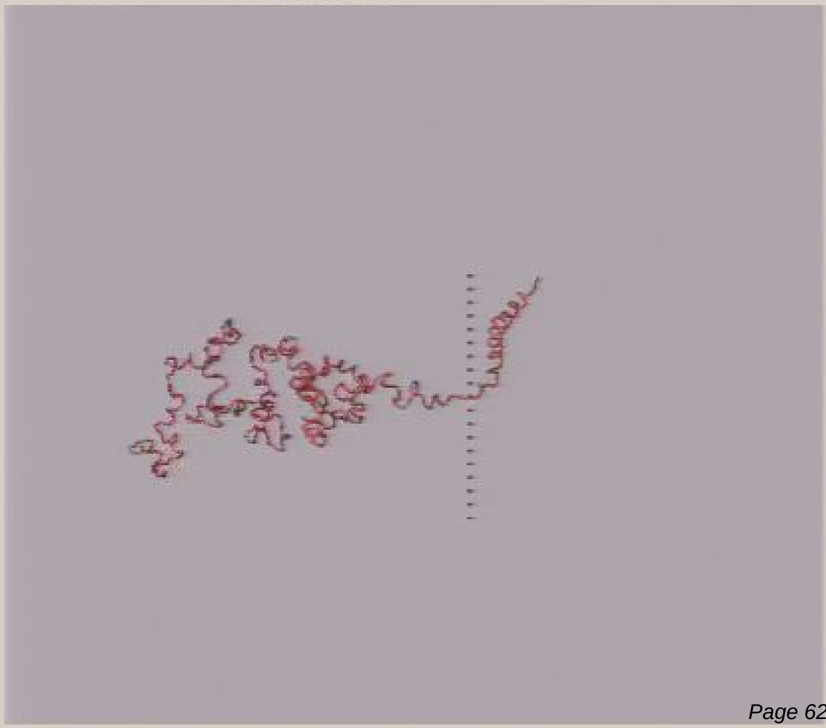

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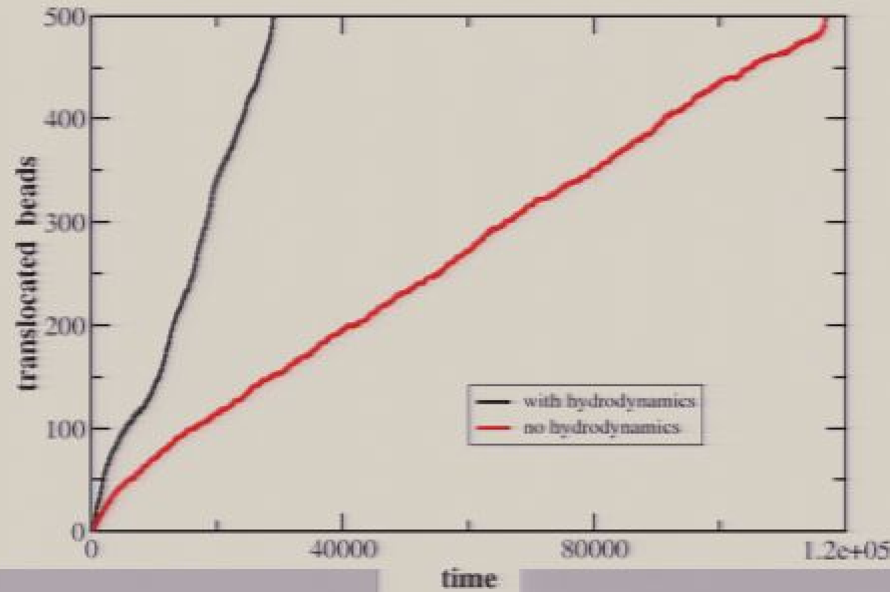
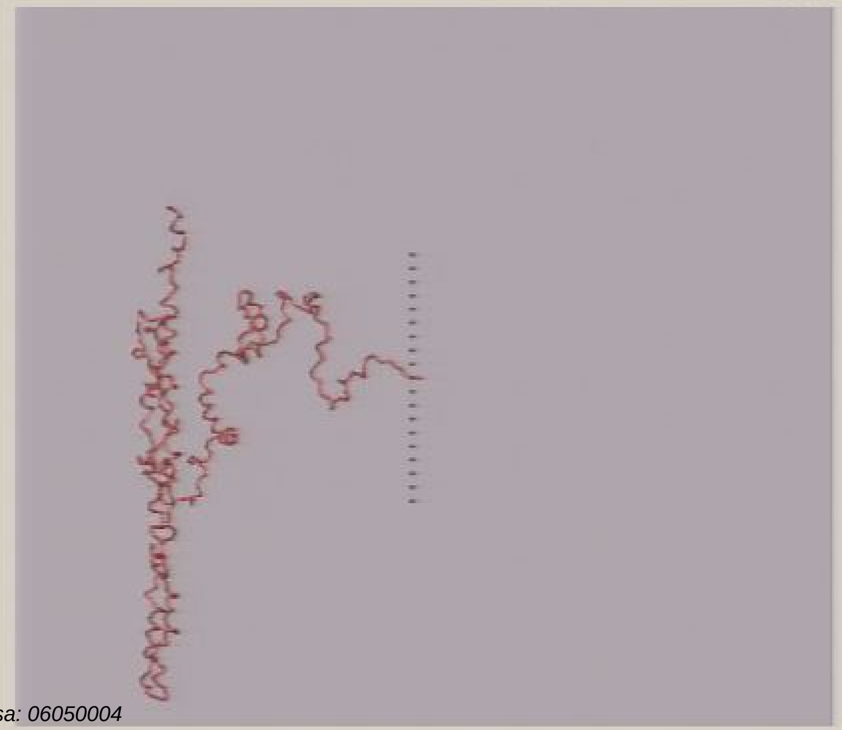
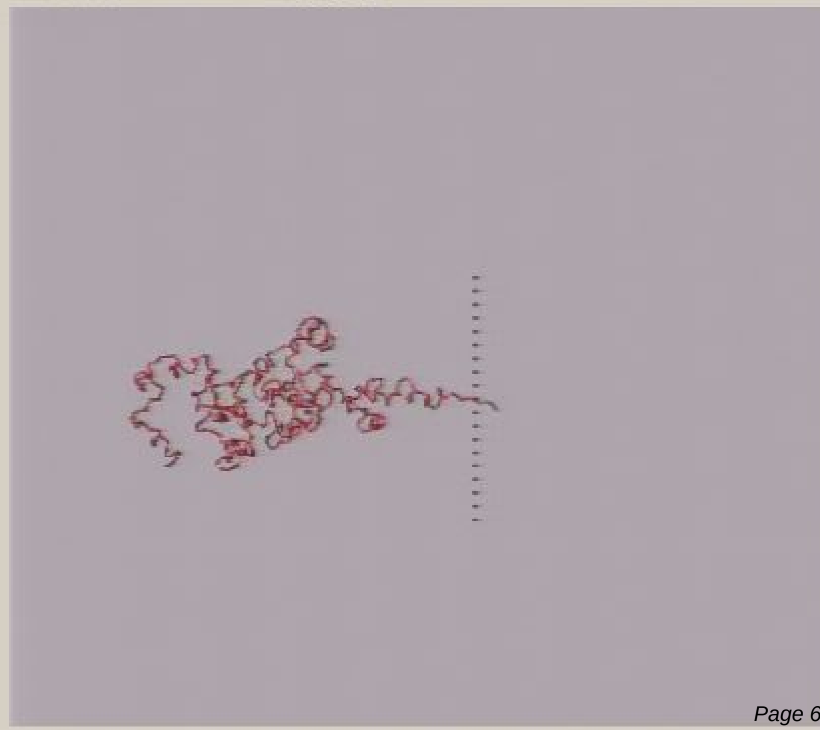
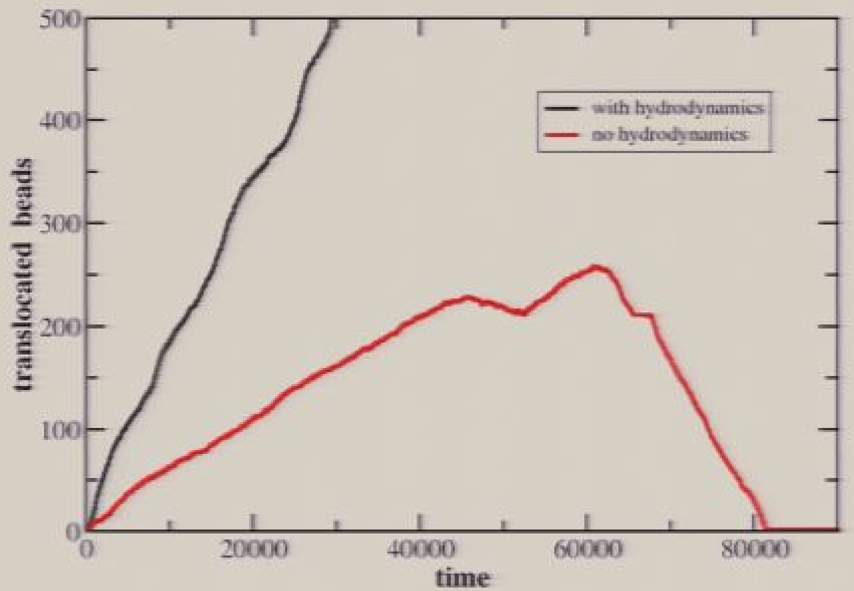






Retraction!



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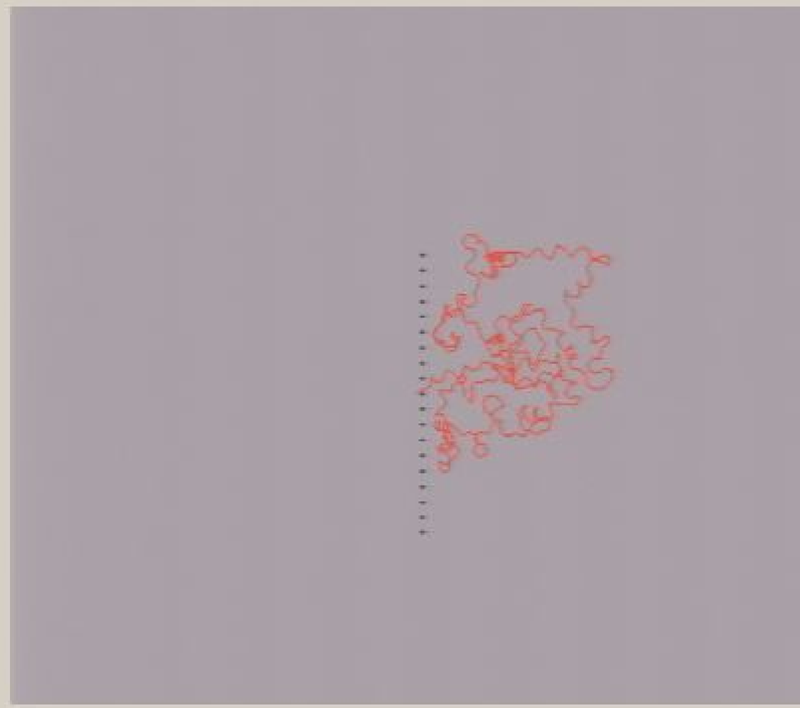
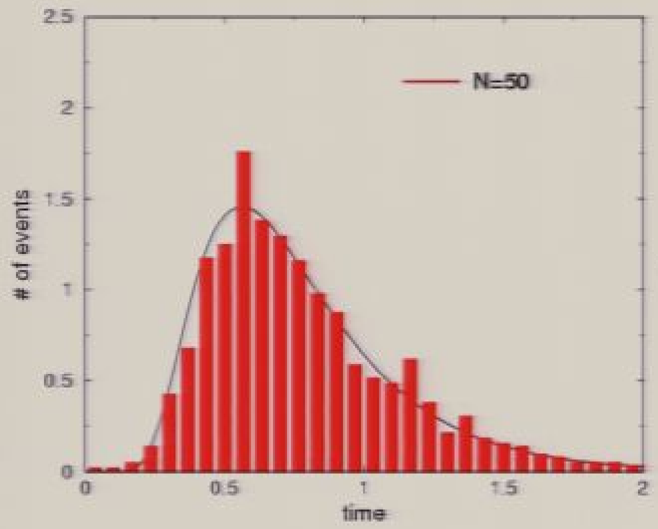
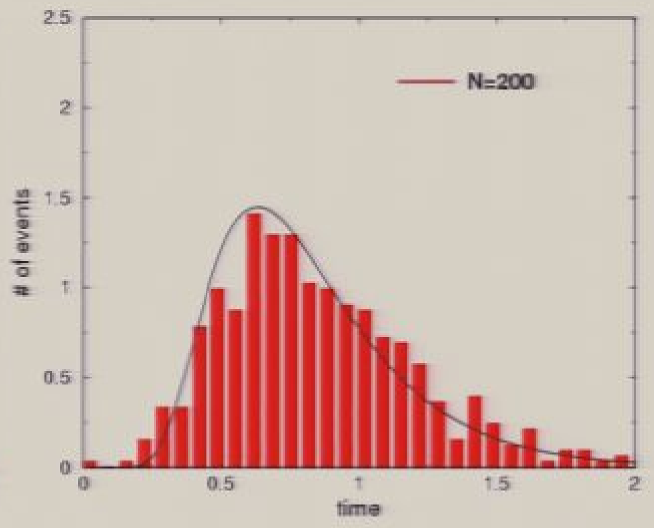
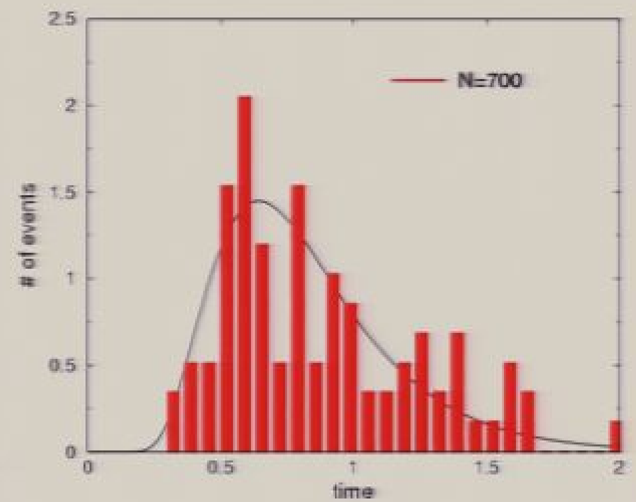
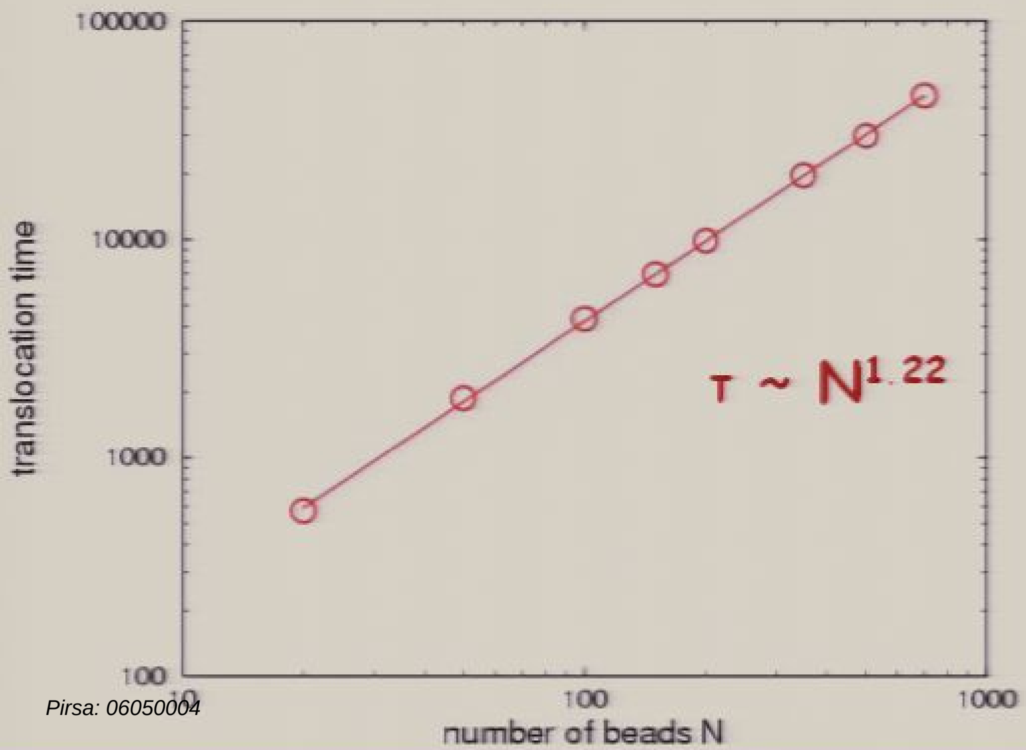


Translocation time - Statistics and scaling









Experiment: $\tau \sim N^{1.27\pm0.03}$

EK GROUP :

Ellad Tadmor (Technion, Israel)
Umesh Waghmare (JNCASR, India)
Hanchul Kim (KRISS, Korea)
Noam Bernstein (NRL, Washington DC)
Greg Smith (Hunter College, NYC)
Olivier Politano (U of Bourgogne, France)
Daniel Orlikowski (LLNL, Livermore, CA)
Dionisios Margetis (Math Dept. MIT)
Ioannis Remediakis (DTU, Denmark)
Gang Lu (CSUN, Northridge, CA)
Nick Choly (FinLabs, Cambridge)
Paul Maragakis (Harvard, Chemistry)
Argyrios Tsolakidis (Shell Oil, Netherlands)
Ryan Barnett
Yina Mo
Su Ying Quek
Sheng Meng
Wenguang Zhu
Maria Fyta
Tom Baker

COLLABORATIONS :

Michael Duesbery (FMR)
Farid Abraham (IBM)
Jeremy Broughton (NRL)
Thomas Frauenheim (U Paderborn)
Marcus Elstner (U Paderborn)
Pantelis Kelires (U of Crete)
Qiang Cui (U of Wisconsin)
Martin Karplus (Harvard)
Weitao Yang (North Carolina)
Zhenyu Zhang (Oak Ridge NL)
Emily Carter (UCLA)
Weinan E (Princeton)
Sauro Succi (U Rome)
Simone Melchionna (U Rome)

SUPPORT: Harvard Nanoscale Science & Engineering Center (NSF), Institute for Theory of Advanced Materials for Information Technology (NSF) AFOSR (Brown MURI), Computational Materials Science Network (DOE)


Harvard Yard, Christmas 2005