1.021, 3.021, 10.333, 22.00 Introduction to Modeling and Simulation
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How to model chemical interactions (cont'd)

Lecture 9

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Content overview

I. Fundamentals of particle methods

1. Atoms, molecules, chemistry
2. Statistical mechanics
3. Molecular dynamics, Monte Carlo
4. Visualization and data analysis
5. Mechanical properties – application: how things fail (and how to prevent it)
6. Multi-scale modeling paradigm
7. Biological systems (simulation in biophysics) – how proteins work and how to model them

II. Advanced topics in particle methods

1. Quantum Weirdness: The Theory of Quantum Mechanics
2. The Many-Body Problem: From Many-Body to Single-Particle
3. Quantum modeling of materials
4. From Atoms to Solids
5. Basic properties of materials
6. Advanced properties of materials
7. Materials Informatics

Lecture 9: Protein mechanics

Outline:

1. Brief review: Force fields for proteins
2. Molecular mechanics of proteins
      2.1 How to apply load to a molecule
3. Preview: Reactive force fields

Goal of today's lecture:

- Deepen our understanding of force fields for proteins and similar materials

- Develop and apply tools in molecular mechanics

1. Brief review: Force fields for proteins

Overview: potential energy models

- **Empirical models: mathematical functions with parameters (fitted to experiment or quantum mechanics)**
    - Pair potentials (LJ, Morse, Buck., harmonic)
    - Embedded atom models/effective medium theories
    - Multi-body potentials (e.g. Tersoff, CHARMM, etc.)
    - Reactive potentials (ReaxFF)

- Semi-empirical models (explicitly note electronic structure)
    - Tight binding
    - MINDO (=Modified Intermediate Neglect of Differential Overlap), NINDO (=Intermediate Neglect of Differential Overlap)

- Quantum mechanical models: Start from Schroedinger's equation (and make approximations to be able to solve it)
    - Quantum chemistry (Hartree-Fock)
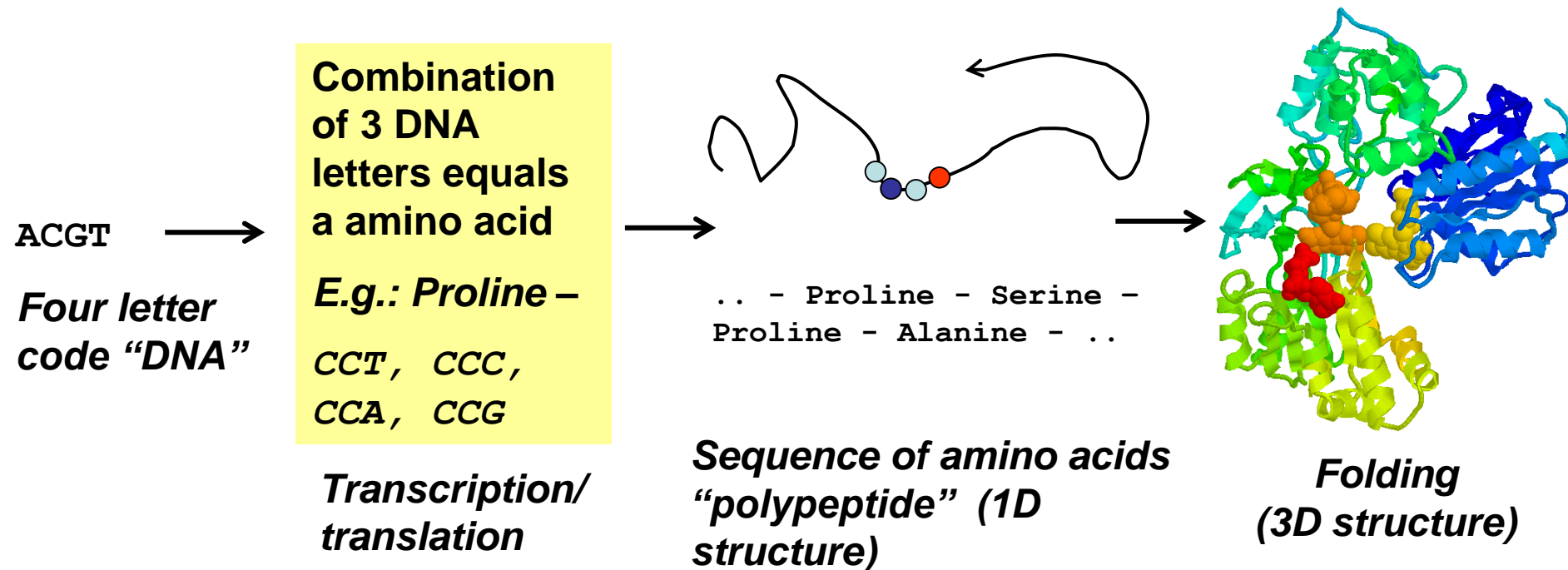   - Density Functional Theory
    - Quantum Monte Carlo

Computational efficiency →

Increased accuracy & "**transferability**" →
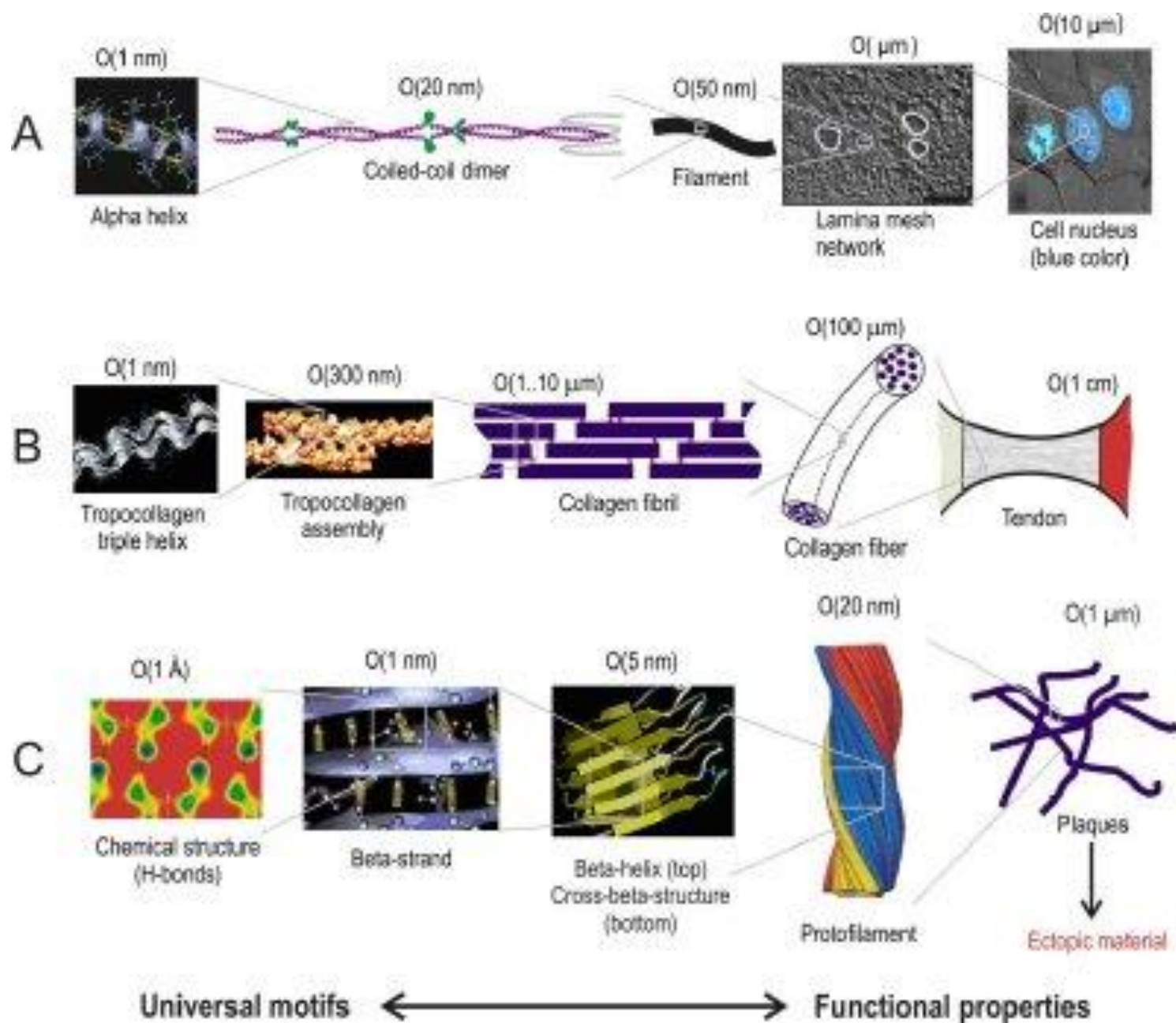
Energy only (and positions, velocities etc.)

Energy and electronic structure

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How protein materials are made – the genetic code

- Proteins: Encoded by DNA (three "letters"), utilize 20 basic building blocks (amino acids) to form polypeptides

- Polypeptides arrange in complex folded 3D structures with specific properties

1D structure transforms into complex 3D folded configuration

`ACGT`

Four letter code "DNA"

Combination of 3 DNA letters equals a amino acid

E.g.: Proline –

CCT, CCC, CCA, CCG

Transcription/ translation

`.. - Proline - Serine – Proline - Alanine - ..`

Sequence of amino acids "polypeptide" (1D structure)

Folding (3D structure)

A

O(1 nm) — Alpha helix

O(20 nm) — Coiled-coil dimer

O(50 nm) — Filament

O(μm) — Lamina mesh network

O(10 μm) — Cell nucleus (blue color)

B

O(1 nm) — Tropocollagen triple helix

O(300 nm) — Tropocollagen assembly

O(1..10 μm) — Collagen fibril

O(100 μm) — Collagen fiber

O(1 cm) — Tendon

C

O(1 Å) — Chemical structure (H-bonds)

O(1 nm) — Beta-strand

O(5 nm) — Beta-helix (top) Cross-beta-structure (bottom)

O(20 nm) — Protofilament

O(1 μm) — Plaques → Ectopic material

Universal motifs ◄——► Functional properties

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Review: atomic interactions – different types of chemical bonds

- **Primary bonds ("strong")**
    - Ionic (ceramics, quartz, feldspar - **rocks**)
    - Covalent (**silicon**)
    - Metallic (copper, nickel, **gold**, silver)
      (high melting point, 1000-5,000K)

- **Secondary bonds ("weak")**
    - Van der Waals (**wax**, low melting point)
    - Hydrogen bonds (proteins, **spider silk**)
      (melting point 100-500K)

- Ionic: Non-directional (point charges interacting)
- Covalent: Directional (bond angles, torsions matter)
- Metallic: Non-directional (electron gas concept)

Difference of material properties originates from different atomic Interactions: Concept: add different contributions (linear addition…)

Summary: CHARMM force field

$$U_{total} = U_{\text{Elec}} + U_{\text{Covalent}} + U_{\text{Metallic}} + U_{\text{vdW}} + U_{\text{H-bond}}$$

=0 for proteins

U_{Elec} : Coulomb potential $\phi(r_{ij}) = \dfrac{q_i q_j}{\varepsilon_1 r_{ij}}$

$U_{\text{Covalent}} = U_{\text{stretch}} + U_{\text{bend}} + U_{\text{rot}} \begin{cases} \phi_{\text{stretch}} = \dfrac{1}{2} k_{\text{stretch}} (r - r_0)^2 \\[2mm] \phi_{\text{bend}} = \dfrac{1}{2} k_{\text{bend}} (\theta - \theta_0)^2 \\[2mm] \phi_{\text{rot}} = \dfrac{1}{2} k_{\text{rot}} (1 - \cos(\vartheta)) \end{cases}$

U_{vdW} : LJ potential $\phi(r_{ij}) = 4\varepsilon \left[\left(\dfrac{\sigma}{r_{ij}} \right)^{12} - \left(\dfrac{\sigma}{r_{ij}} \right)^{6} \right]$
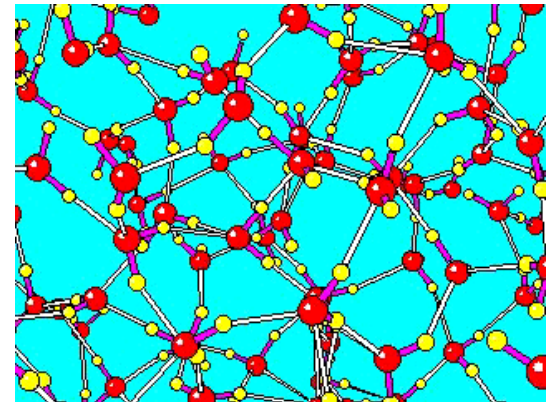
$U_{\text{H-bond}}$: $\phi(r_{ij}) = D_{\text{H-bond}} \left[5 \left(\dfrac{R_{\text{H-bond}}}{r_{ij}} \right)^{12} - 6 \left(\dfrac{R_{\text{H-bond}}}{r_{ij}} \right)^{10} \right] \cos^4(\theta_{\text{DHA}})$

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Common empirical force fields for organics and proteins

Class I (experiment derived, simple form)
- CHARMM
- CHARMm (Accelrys)
- AMBER
- OPLS/AMBER/Schrödinger
- ECEPP (free energy force field)
- GROMOS

Harmonic terms; Derived from vibrational spectroscopy, gas-phase molecular structures
Very system-specific

Class II (more complex, derived from QM)
- CFF95 (Biosym/Accelrys)
- MM3
- MMFF94 (CHARMM, Macromodel…)
- UFF, DREIDING

Include anharmonic terms
Derived from QM, more general

http://www.ch.embnet.org/MD_tutorial/pages/MD.Part2.html
http://www.pharmacy.umaryland.edu/faculty/amackere/force_fields.htm
http://amber.scripps.edu/

2. Molecular mechanics of proteins

How proteins deform and ultimately fail…**physiologically and in disease**
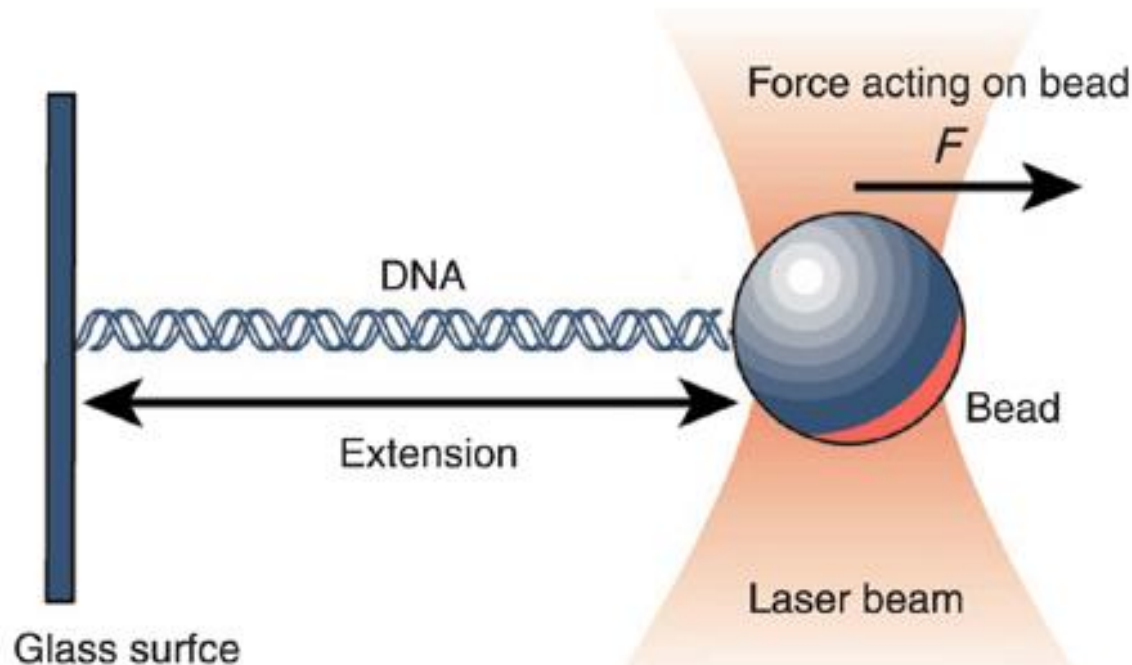
Cooking spaghetti

stiff rods   *cooking*   *soft, flexible rods*
(like many protein molecules)

Single molecule tensile test – "optical tweezer"

molecule

one end of
molecule fixed
at surface

bead trapped
in laser light
(moves with
laser)

tith
molecule

AB 1

AB 2

stage
movement
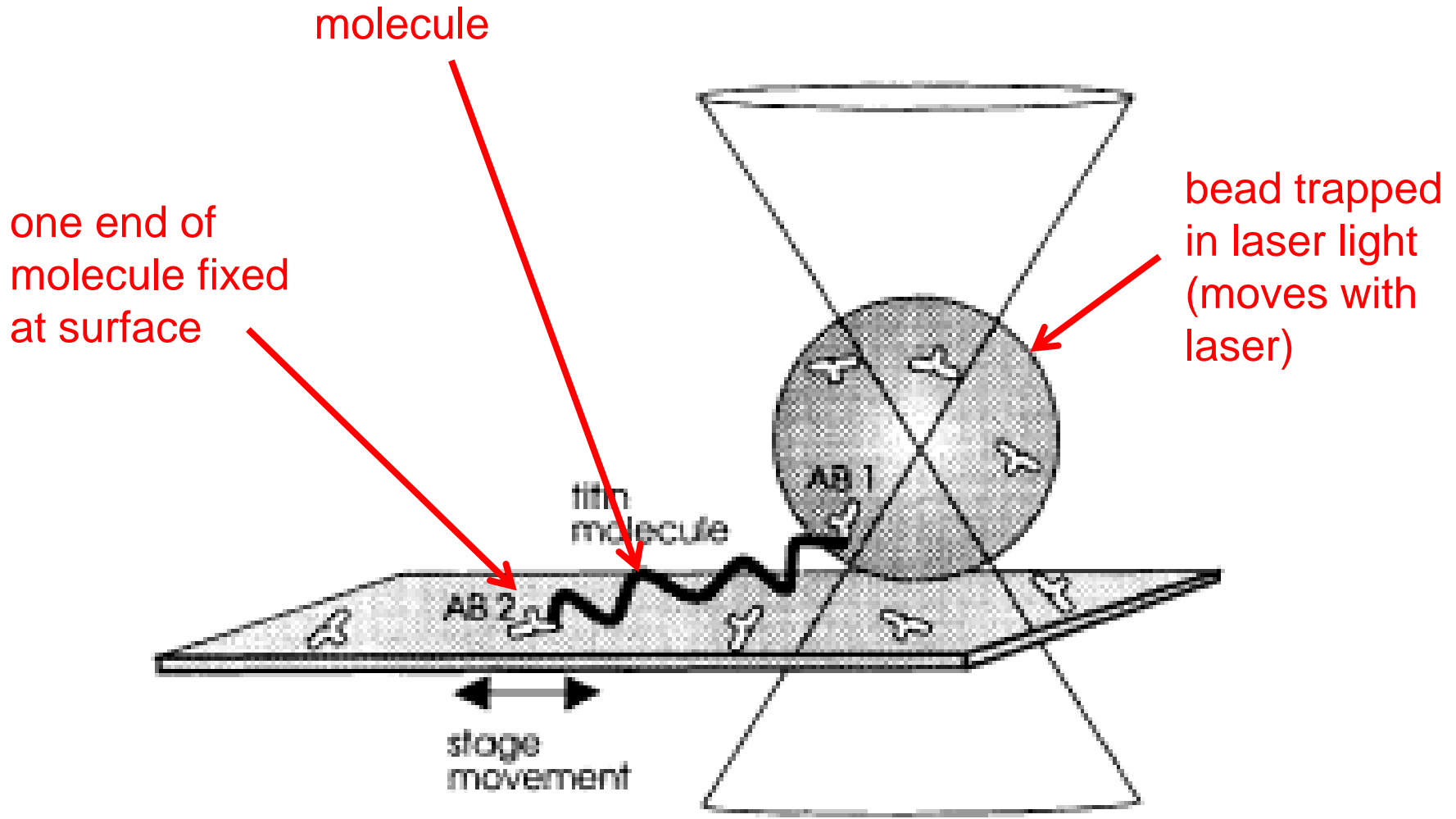
Example 1: Elasticity of tropocollagen molecules

Entropic elasticity leads to strongly nonlinear elasticity

300 nm length
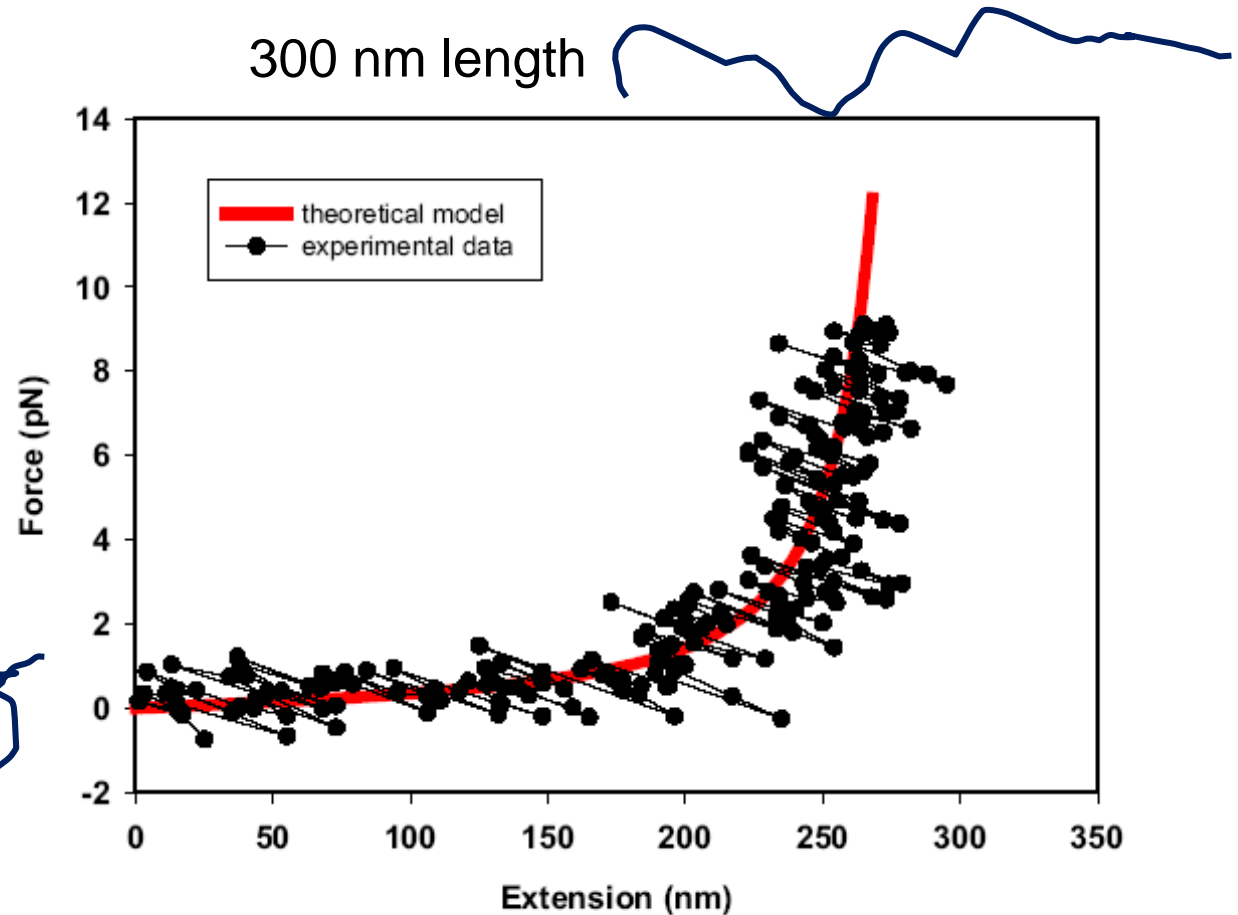
Fig. 2. The force-extension curve for stretching a single type II collagen molecule. The data were fitted to Marko–Siggia entropic elasticity model. The molecule length and persistence length of this sample is 300 and 7.6 nm, respectively.

Sun *et al.*, 2004

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Example 2: Single protein molecule mechanics

Optical tweezers experiment

Protein structure (I27 multidomain titin in muscle)

Experimental techniques

Biological Structures

actin

DNA

DNA, proteins, cytoskeletal elements

nanoparticles

red blood cell

viruses   cells   tissues   organs

Size

| 1nm | 100nm | 1μm | 1mm | 1cm | 1m |

Experimental Techniques

Nanoindention

Atomic force microscopy

Molecular force spectroscopy

Micropipette aspiration

Optical trap/Laser tweezers

Areas of biomechanics

Single molecule biomechanics, Ligand-receptor interactions, cytoskeletal mechanics

Cell mechanics, cell-substrate interaction

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After: C.T. Lim, 2006

2.1 How to apply load to a molecule

(in molecular dynamics simulations)

Steered molecular dynamics (SMD)

Steered molecular dynamics used to apply forces to protein structures

Virtual atom moves w/ velocity $\vec{v}$

$\vec{v}$

k

$\vec{x}$

end point of molecule

Steered molecular dynamics (SMD)

Steered molecular dynamics used to apply forces to protein structures

Virtual atom moves w/ velocity $\vec{v}$

$$f = k(v \cdot t - x)$$

$$\vec{v} \cdot t - \vec{x}$$
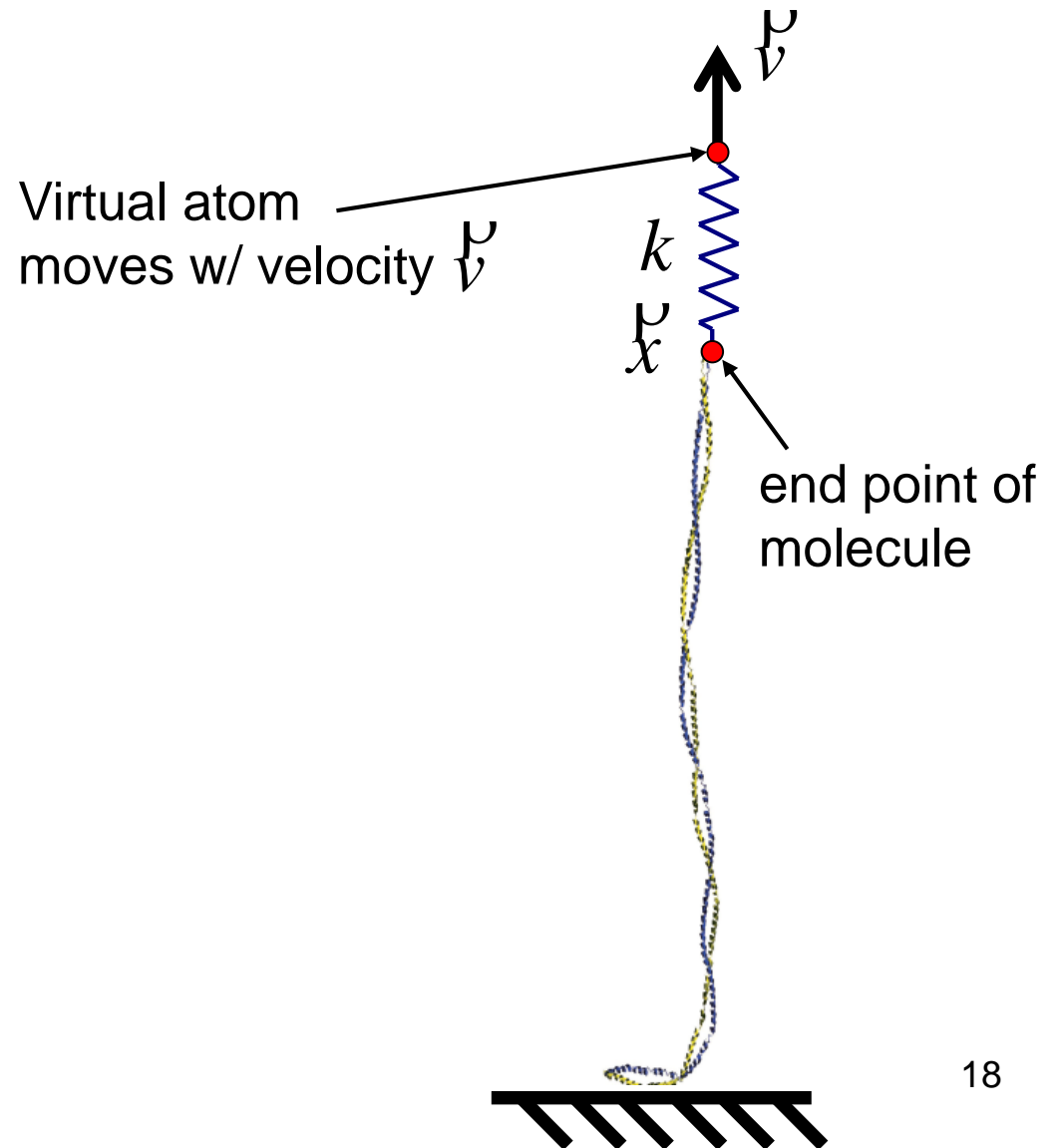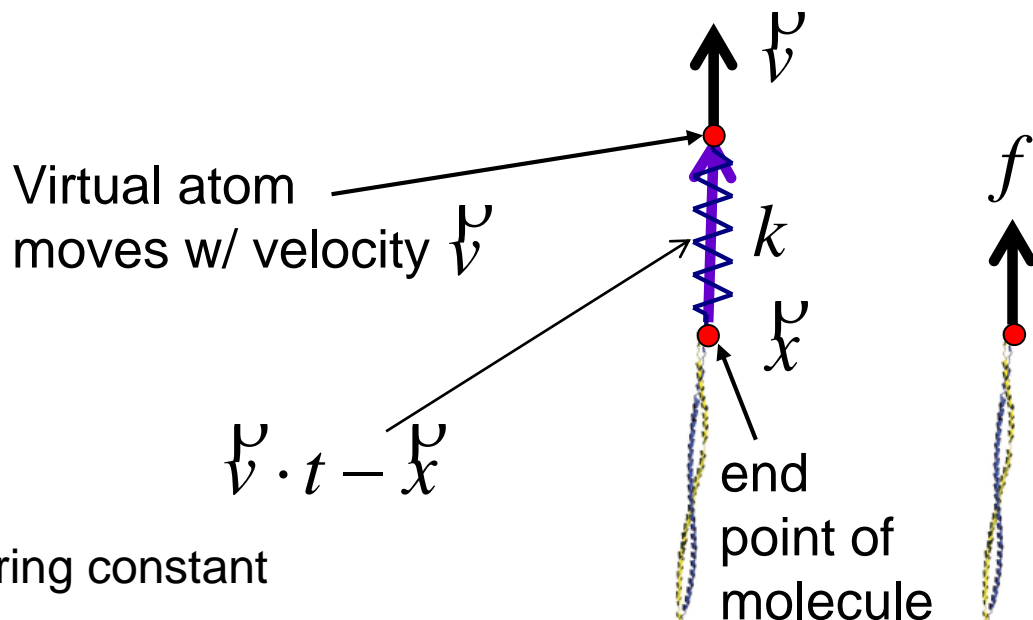
$$\vec{f} = k(\vec{v} \cdot t - \vec{x})$$

SMD spring constant

end point of molecule

SMD deformation speed vector

time

Distance between end point of molecule and virtual atom

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SMD mimics AFM single molecule experiments

Atomic force microscope
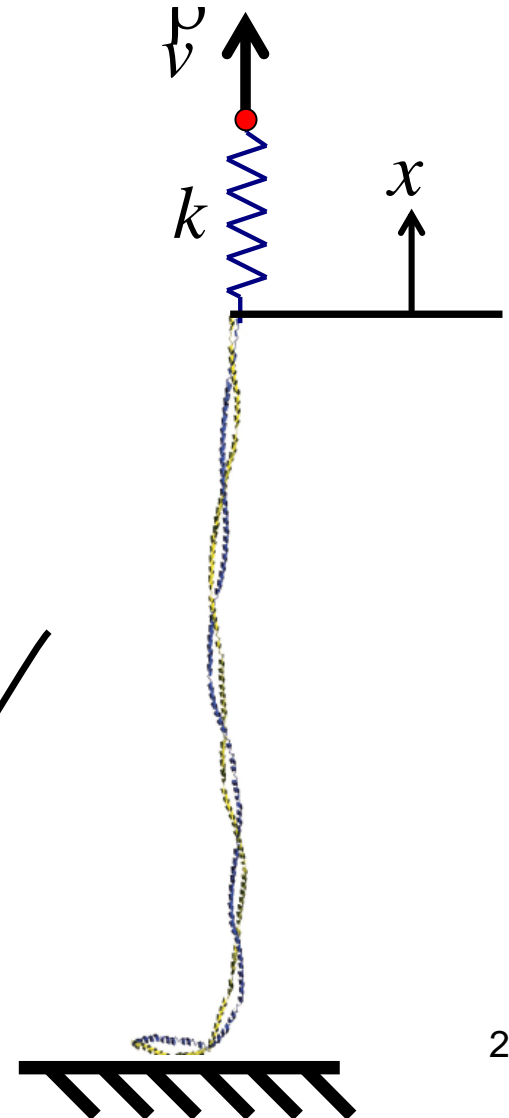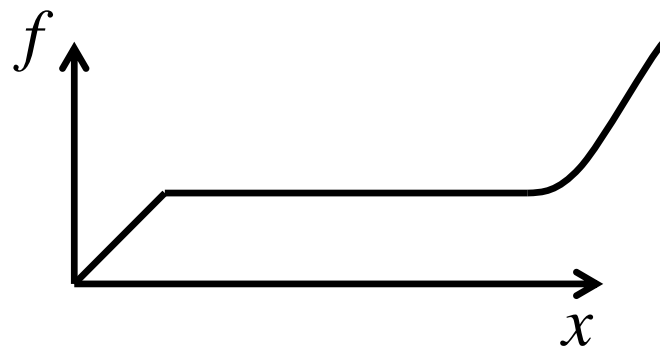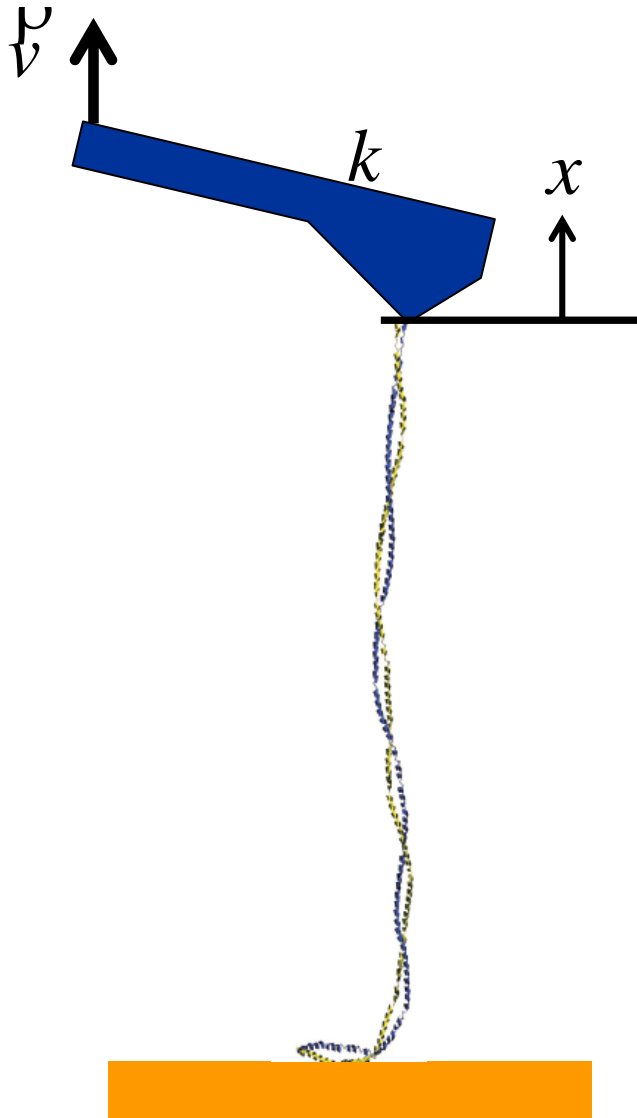
SMD is a useful approach to probe the nanomechanics of proteins (elastic deformation, "plastic" – permanent deformation, etc.)

Example: titin unfolding (CHARMM force field)

Unfolding of titin molecule

Force - Displacement Curve

X: breaking

X

X

Force (pN)

Displacement (A)
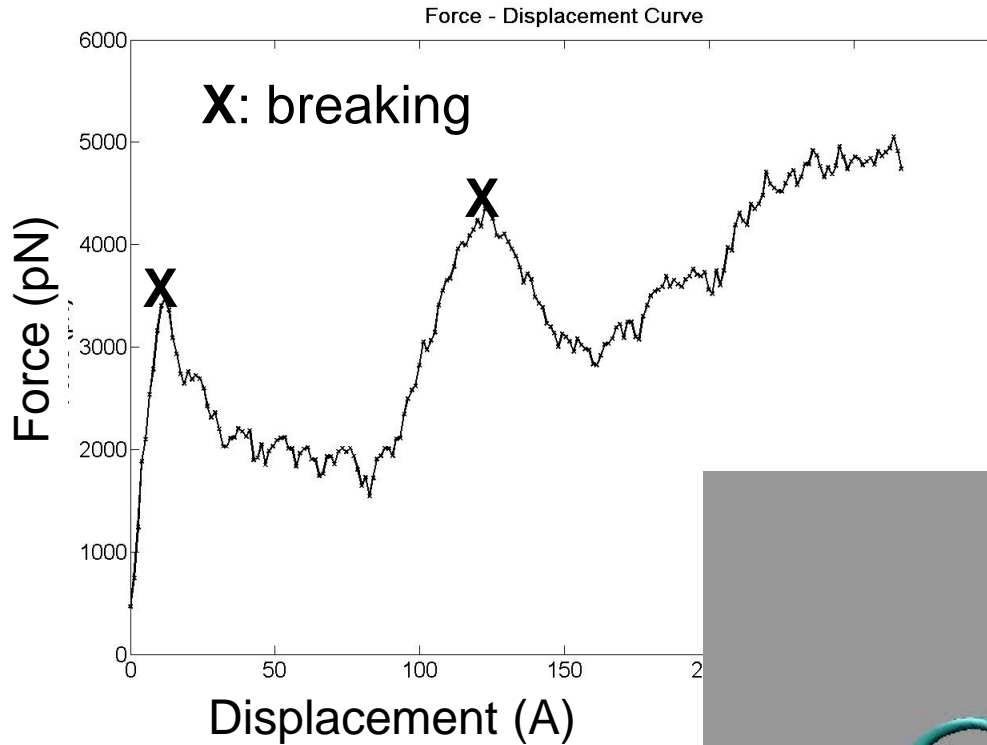
Titin I27 domain: Very resistant to unfolding due to parallel H-bonded strands

Keten and Buehler, 2007
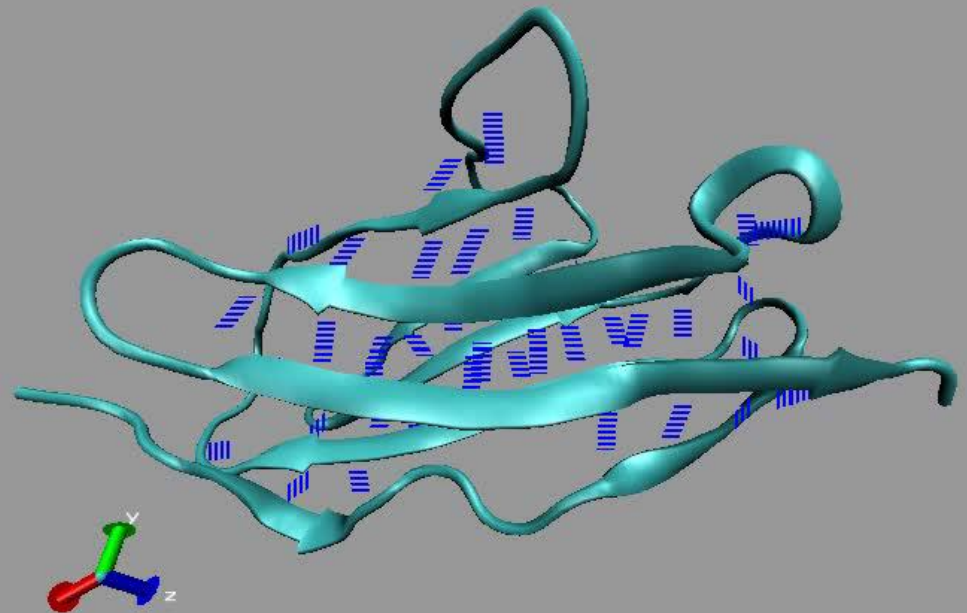
Protein unfolding – reactive model (allows for bond breaking)

F

AHs

F

PnIB 1AKG

(a)

(b) Breaking C-S

A

(c) Breaking S-S

B

(d)

(e)

C

Breaking C-C

ReaxFF modeling

M. Buehler, JoMMS, 2007

Protein unfolding - CHARMM

(a)

(b)

(c)

A

Covalent bonds don't break

(d)

(e)
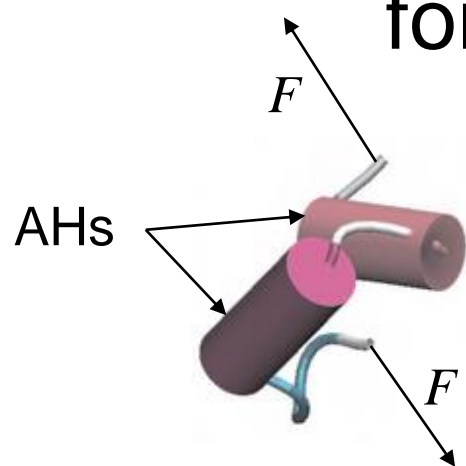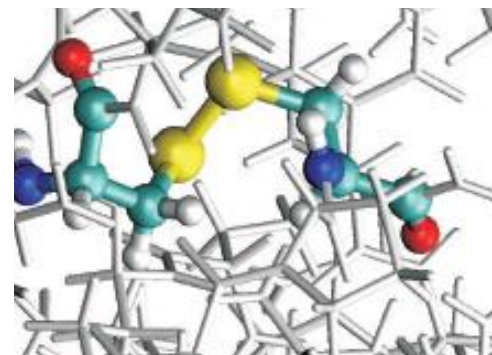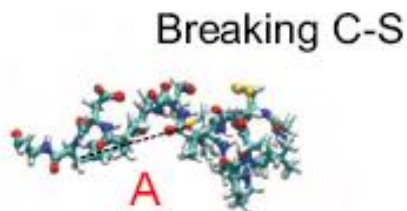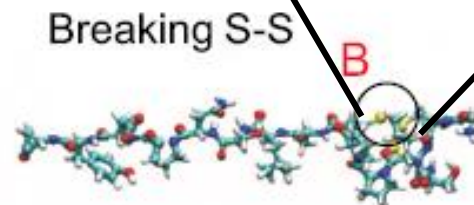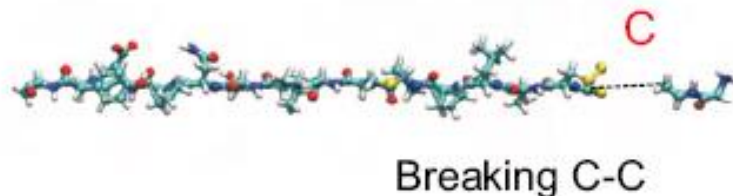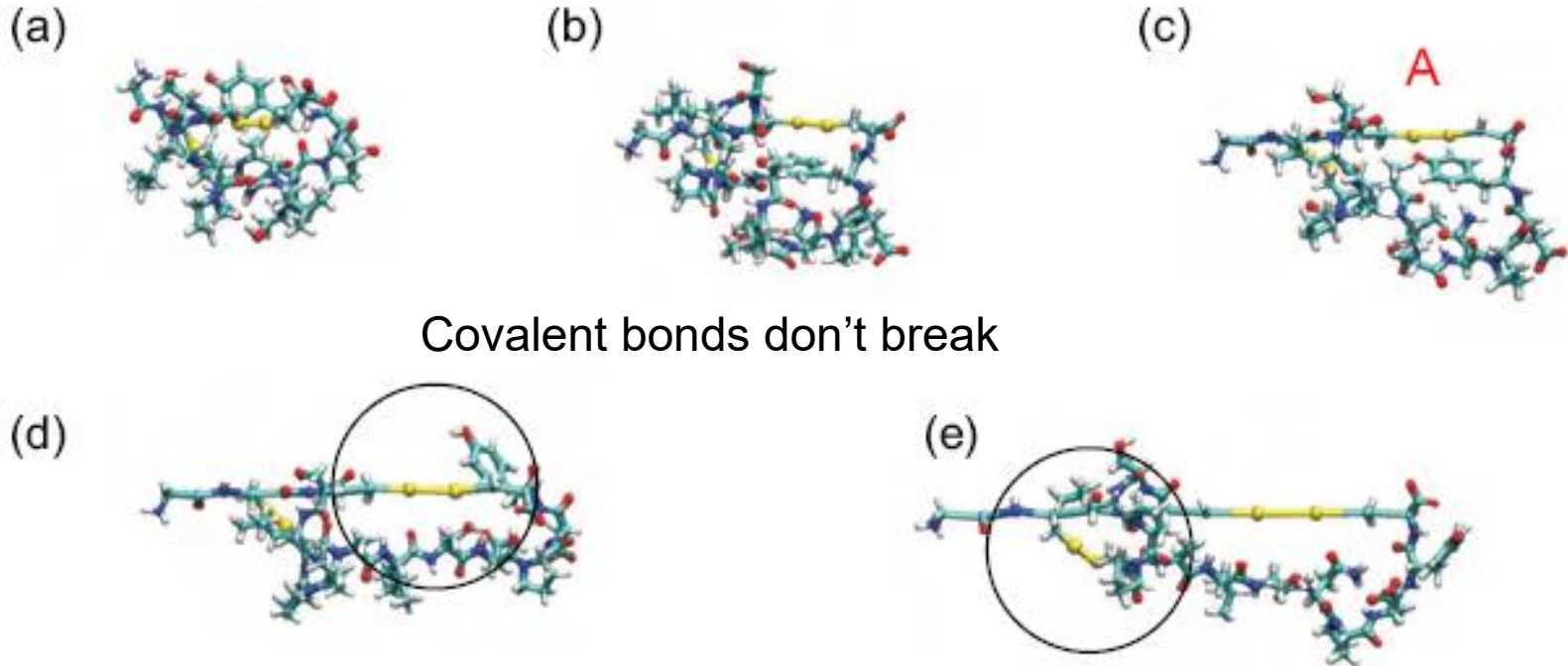
CHARMM modeling

Comparison – CHARMM vs. reactive model (allows for bond breaking)

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M. Buehler, JoMMS, 2007
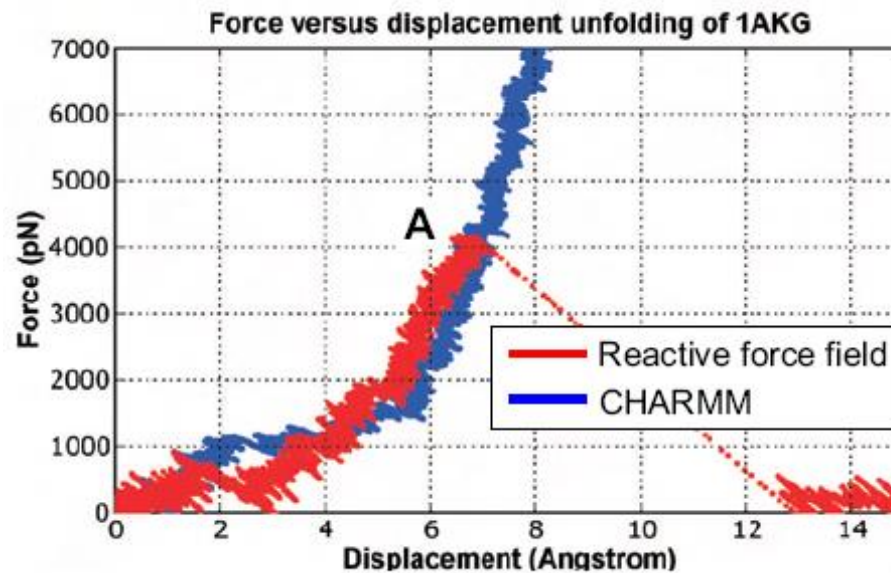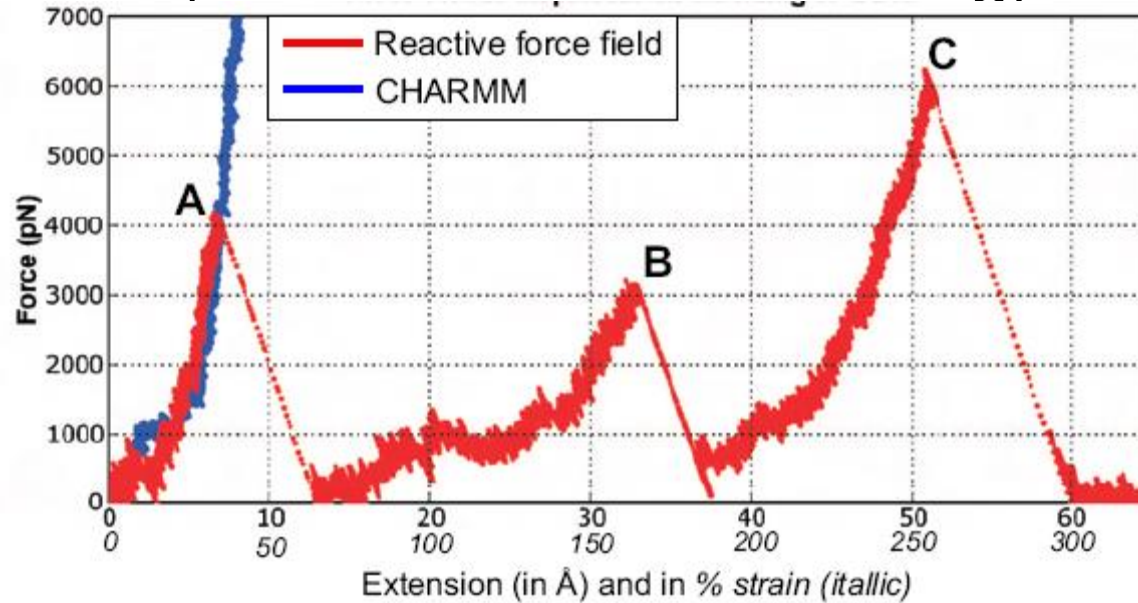
Case study: From nanoscale filaments to micrometer meshworks

Movie: MD simulation of AH coiled coil
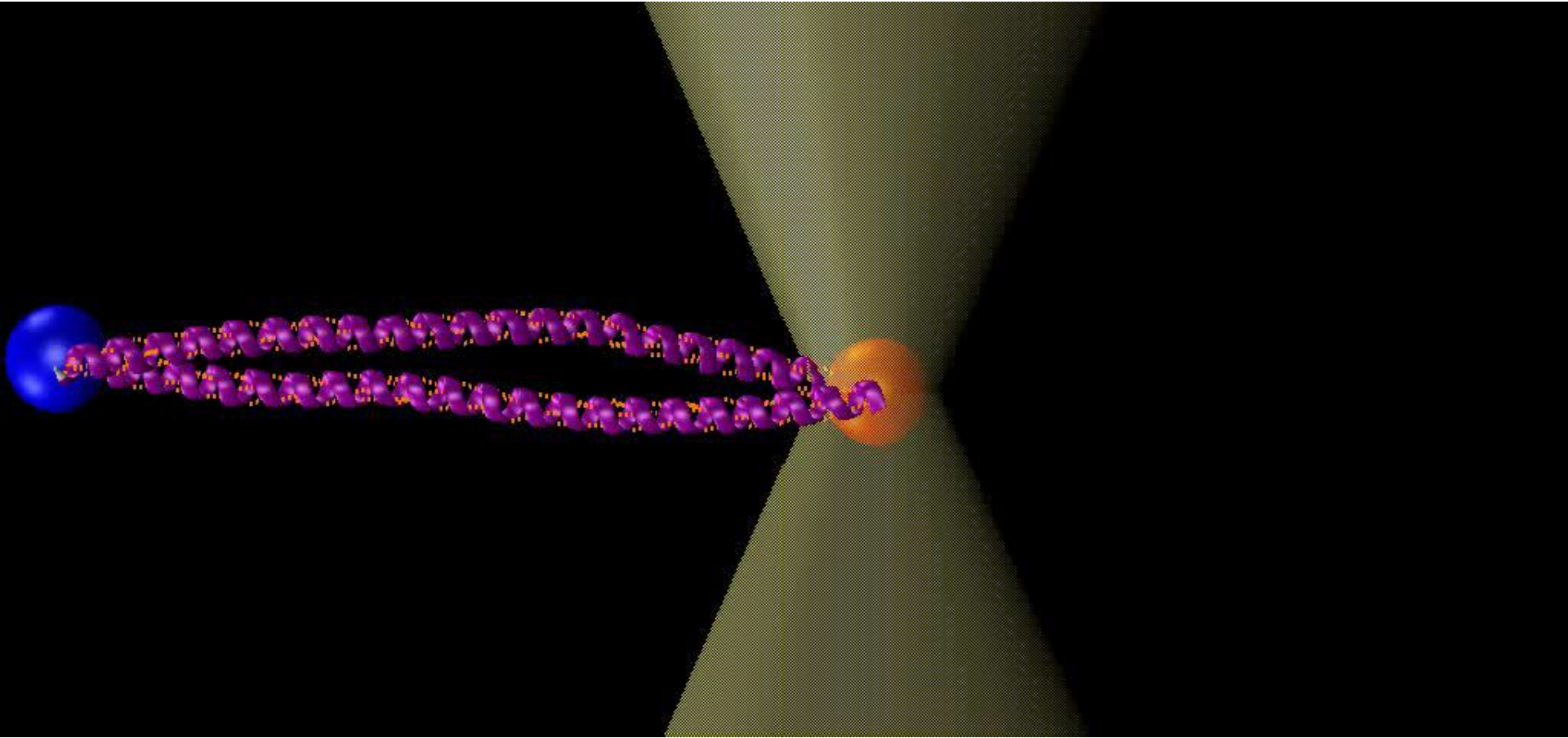
Z. Qin, ACS Nano, 2011
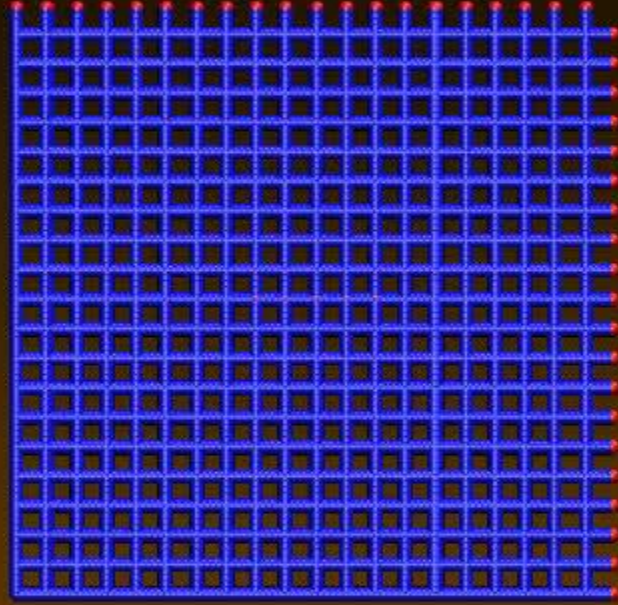
Supersonic fracture in cellular protein meshwork

Z. Qin, BioNanoScience, 2010

What about varying pulling speeds?

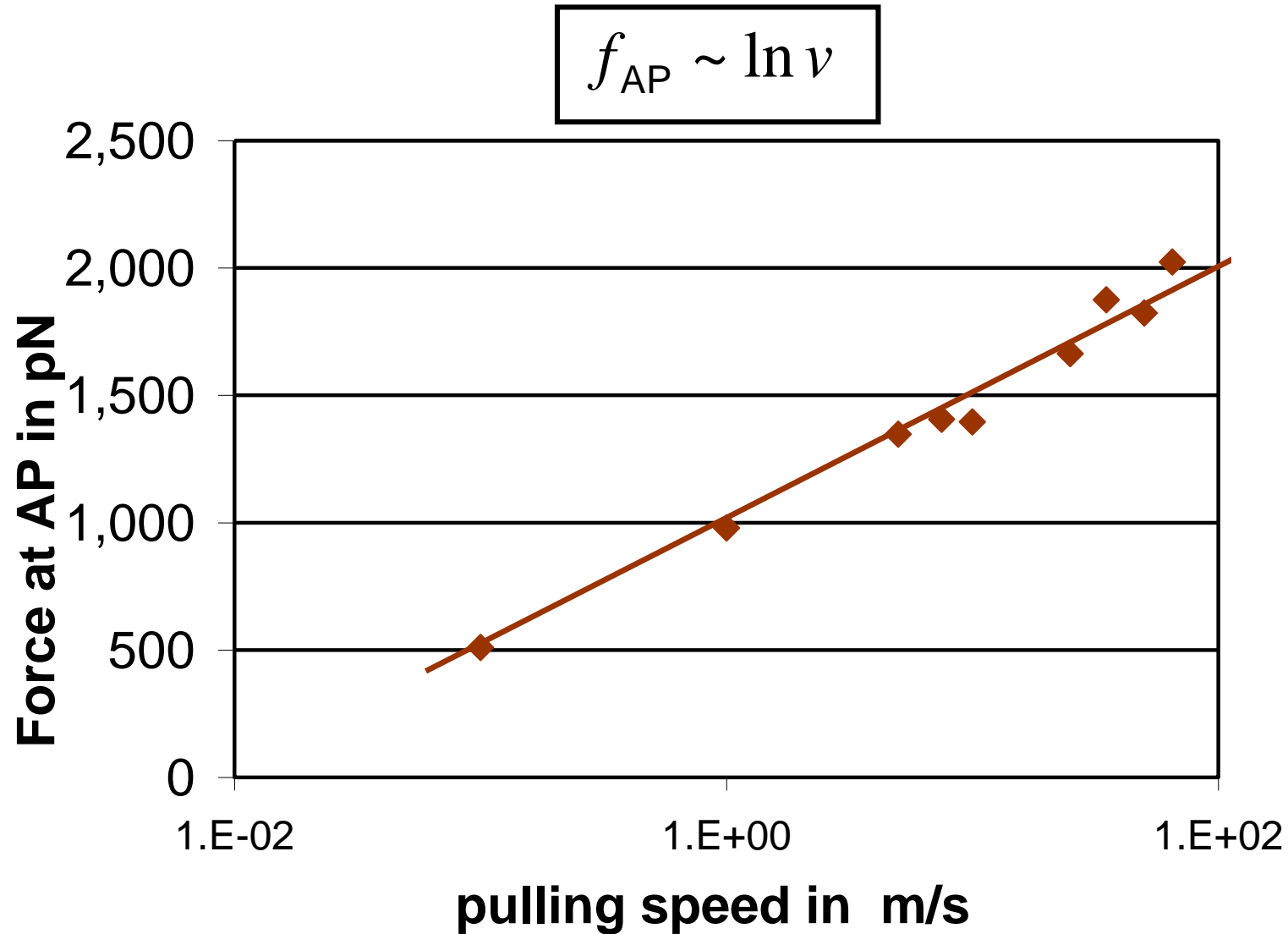*Changing the time-scale of observation of fracture*
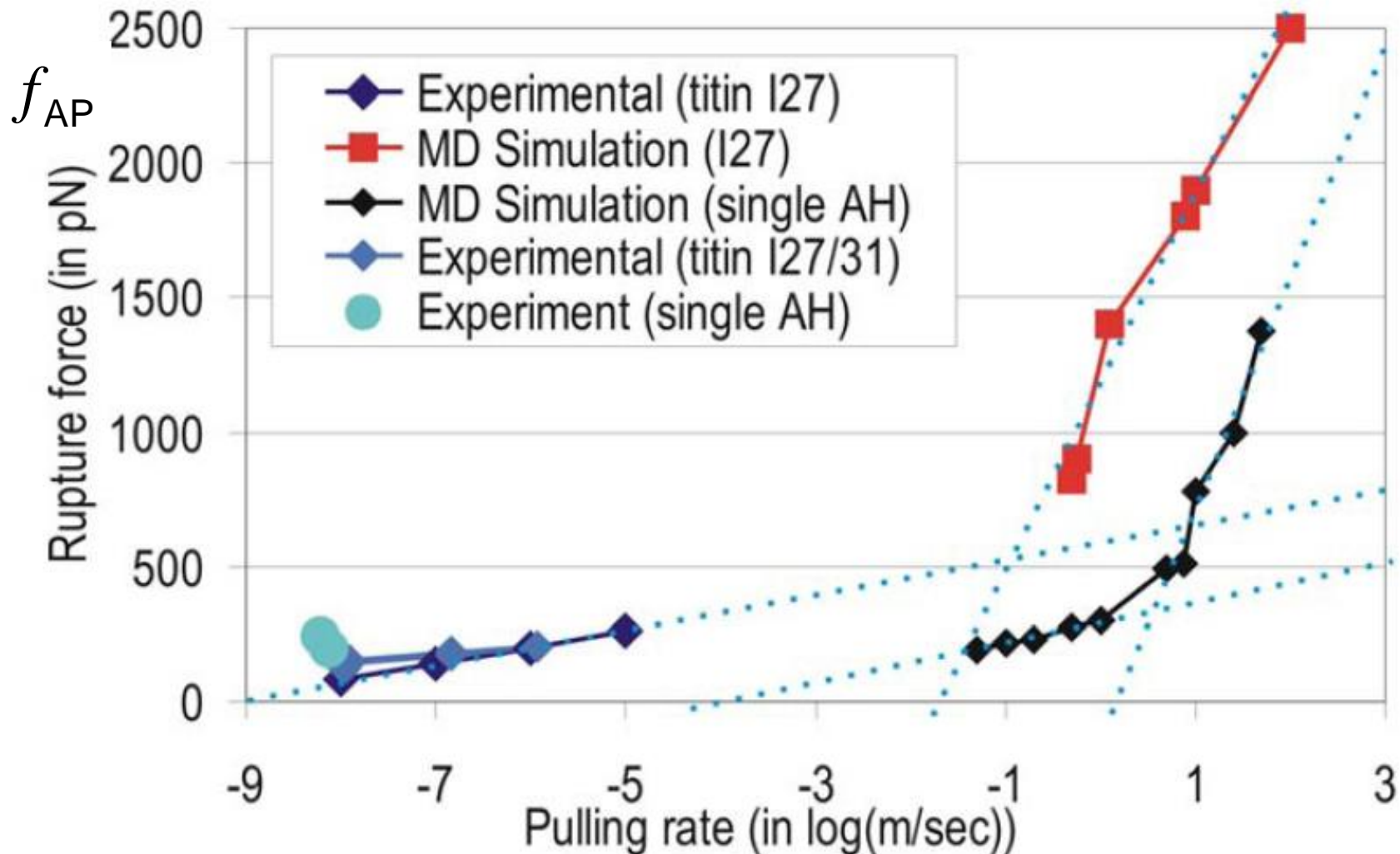
Variation of pulling speed

Ackbarow and Buehler, *J. Mat. Sci.*, 2007
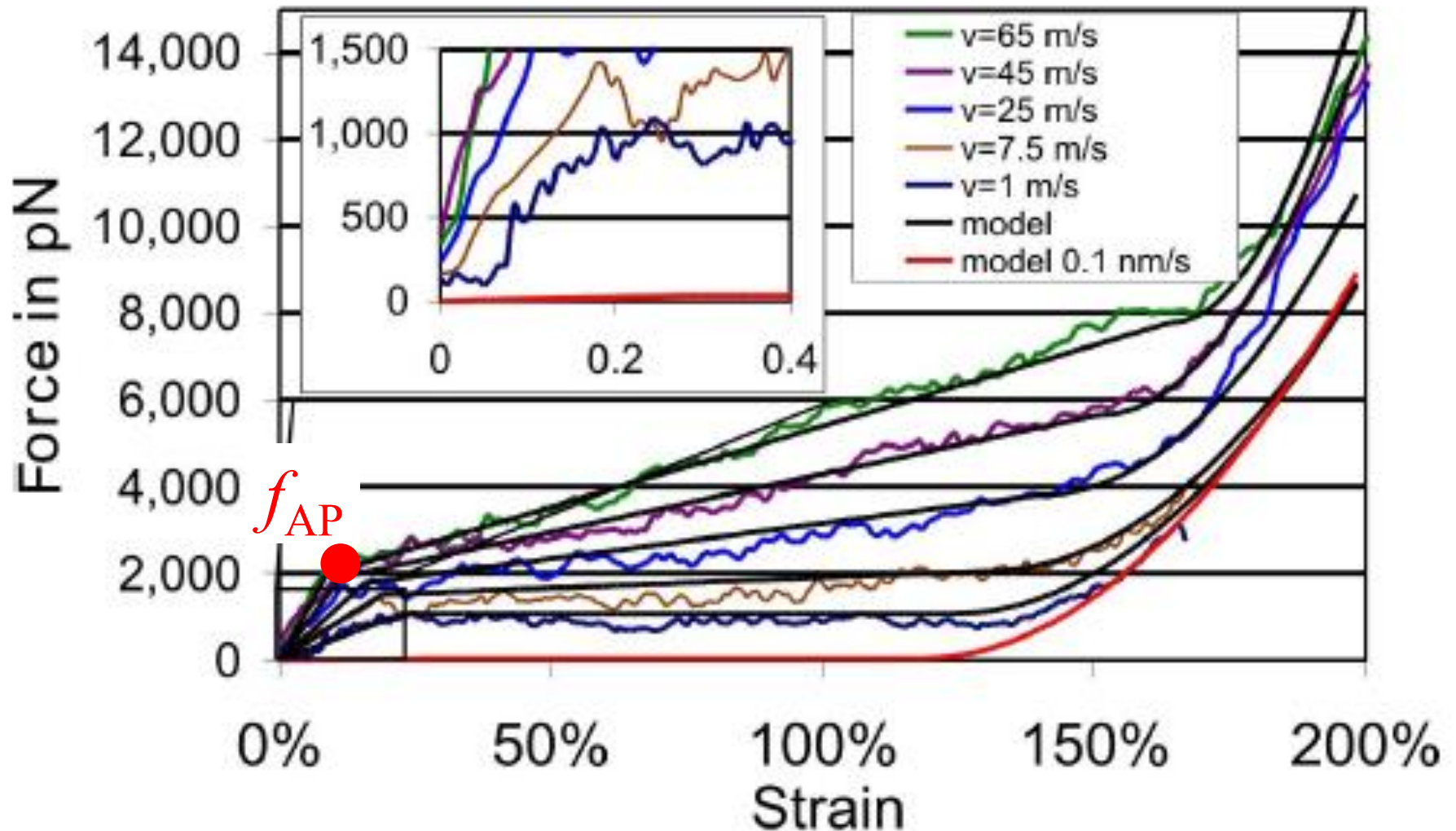
(a) **(b)** **(c)** **(d)**
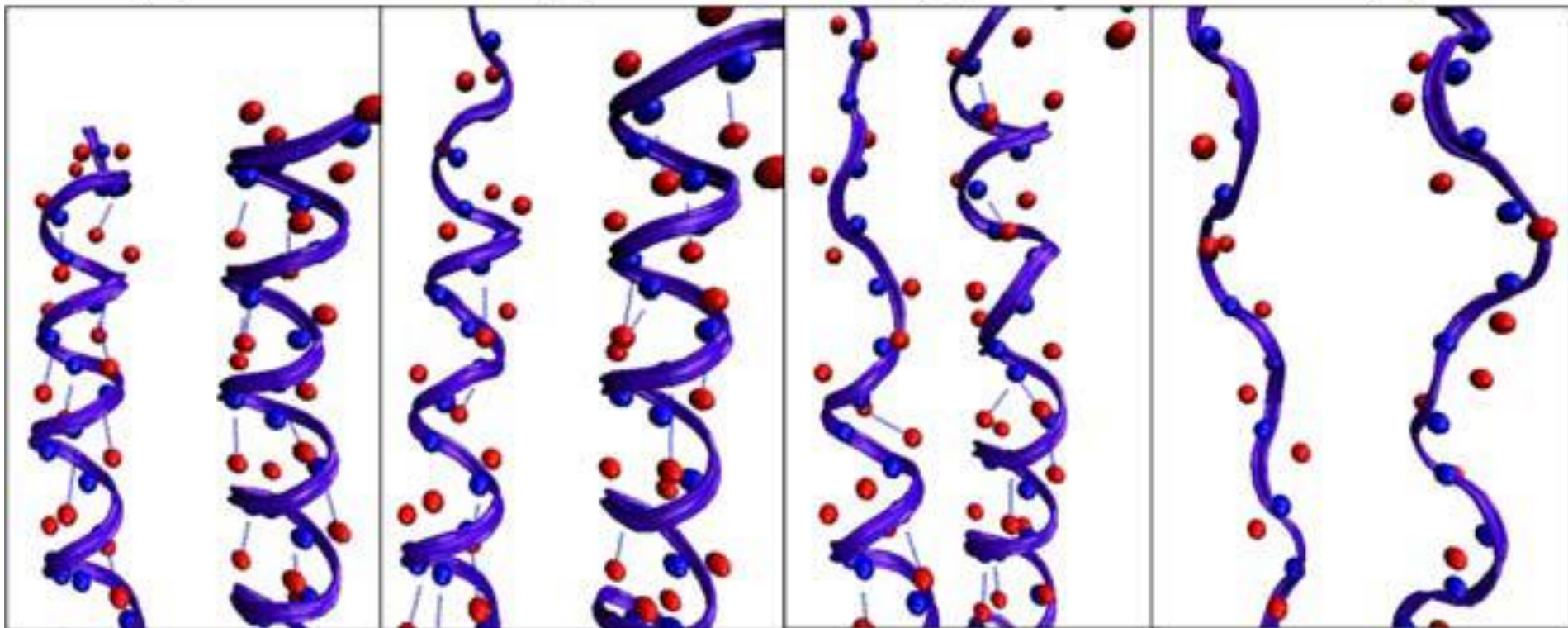
Force at angular point f_{AP}=fracture force

$$f_{AP} \sim \ln v$$

Force at AP in pN vs. pulling speed in m/s

Ackbarow and Buehler, *J. Mat. Sci.*, 2007
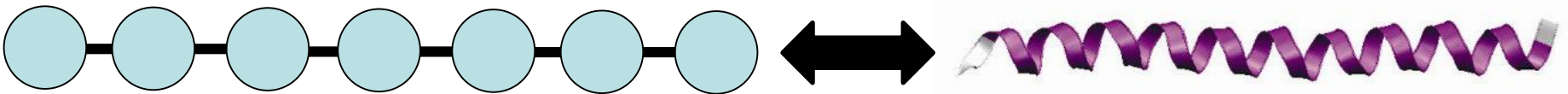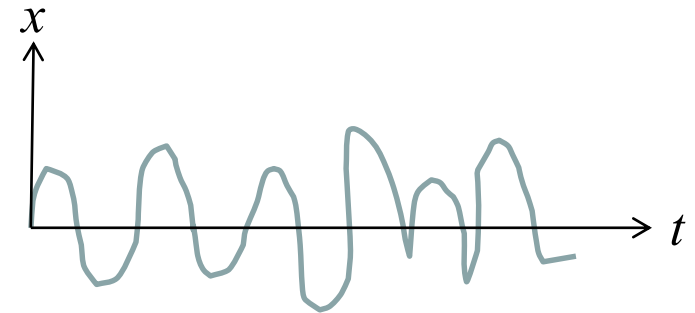
General results…

Rupture force vs. pulling speed

How to make sense of these results?

A few fundamental properties of bonds

- Bonds have a "bond energy" (energy barrier to break)

- Arrhenius relationship gives probability for energy barrier to be overcome, given a temperature

$$p = \exp\left(-\frac{E_b}{k_B T}\right)$$

- All bonds vibrate at frequency ω

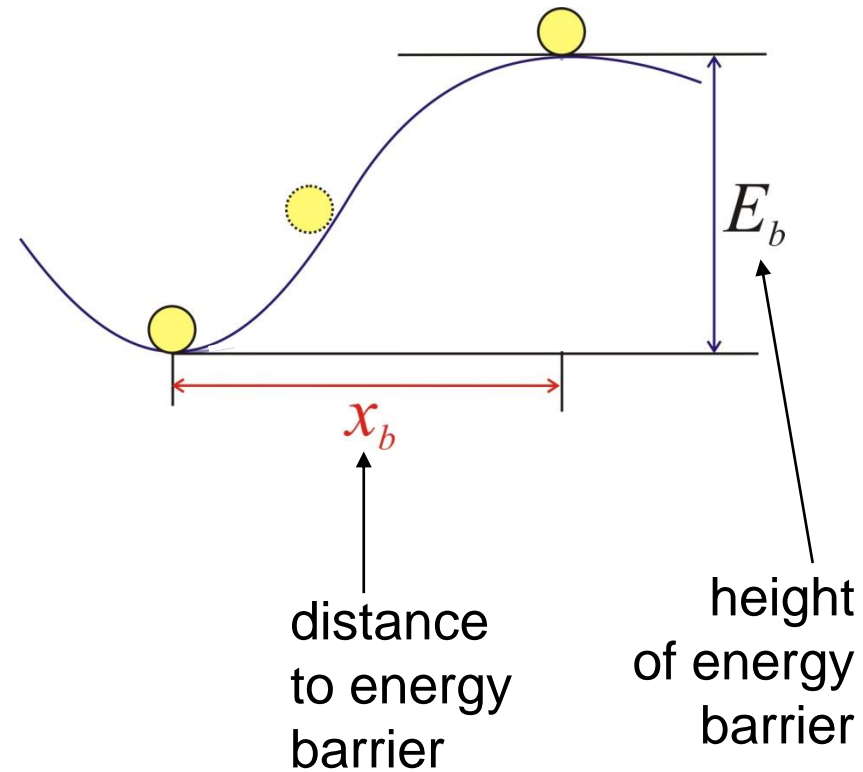# Bell model

Probability for bond rupture (Arrhenius relation)

$$p = \exp\left(-\frac{E_b}{k_B T}\right)$$

Boltzmann constant

temperature

E_b

x_b

distance to energy barrier

height of energy barrier

"bond"

Bell model

Probability for bond rupture (Arrhenius relation) $\quad f = f_{\text{AP}}$

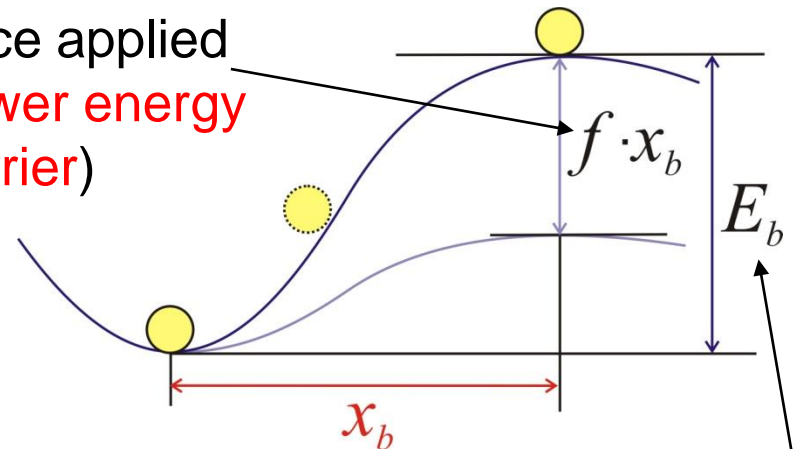$$p = \exp\left(-\frac{E_b - f \cdot x_B}{k_B T}\right)$$

Boltzmann constant

temperature

force applied (lower energy barrier)

$f \cdot x_b$

E_b

x_b

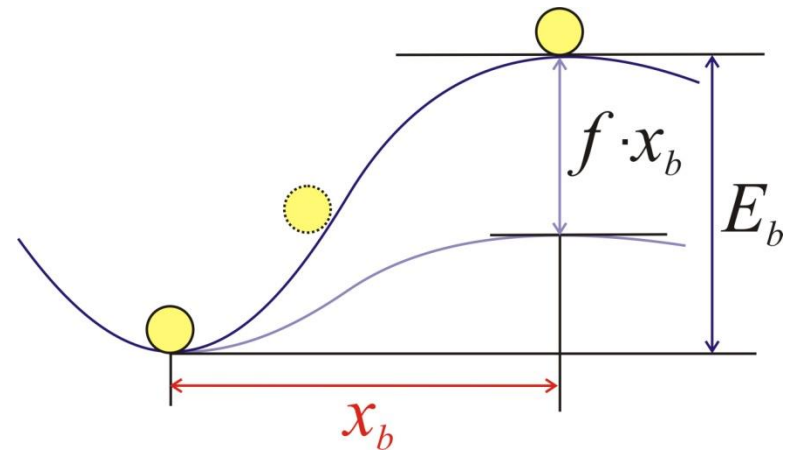distance to energy barrier

height of energy barrier

"bond"

Bell model

Probability for bond rupture (Arrhenius relation)
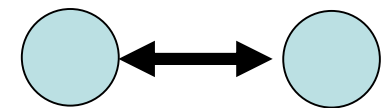
$$p = \exp\left(-\frac{E_b - f \cdot x_B}{k_B T}\right)$$

Off-rate = probability times vibrational frequency

$$\chi = \omega_0 \cdot p$$

$$\omega_0 = 1 \times 10^{13} \, 1/\sec$$

bond vibrations

Bell model
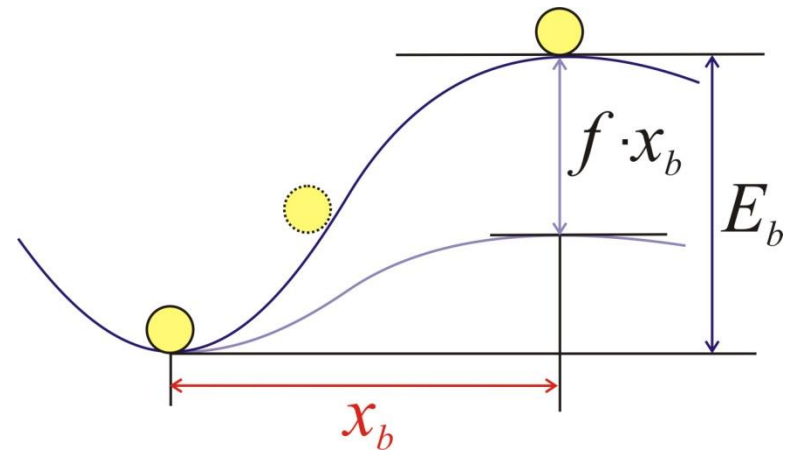
Probability for bond rupture (Arrhenius relation)
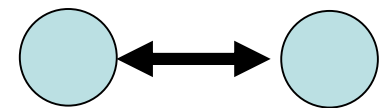
$$p = \exp\left(-\frac{E_b - f \cdot x_B}{k_B T}\right)$$

Off-rate = probability times vibrational frequency

$$\chi = \omega_0 \cdot p = \omega_0 \cdot \exp\left(-\frac{(E_b - f \cdot x_b)}{k_b \cdot T}\right)$$

$$\omega_0 = 1 \times 10^{13} \ 1/\sec$$

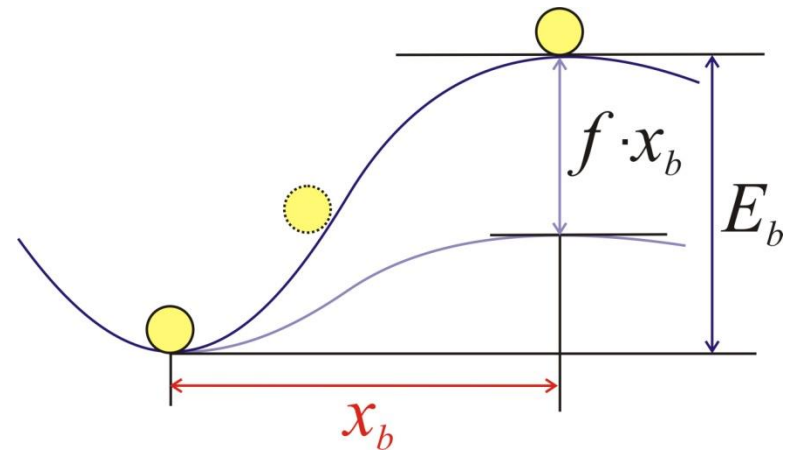*"How often bond breaks per unit time"*

bond vibrations

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Bell model

Probability for bond rupture (Arrhenius relation)
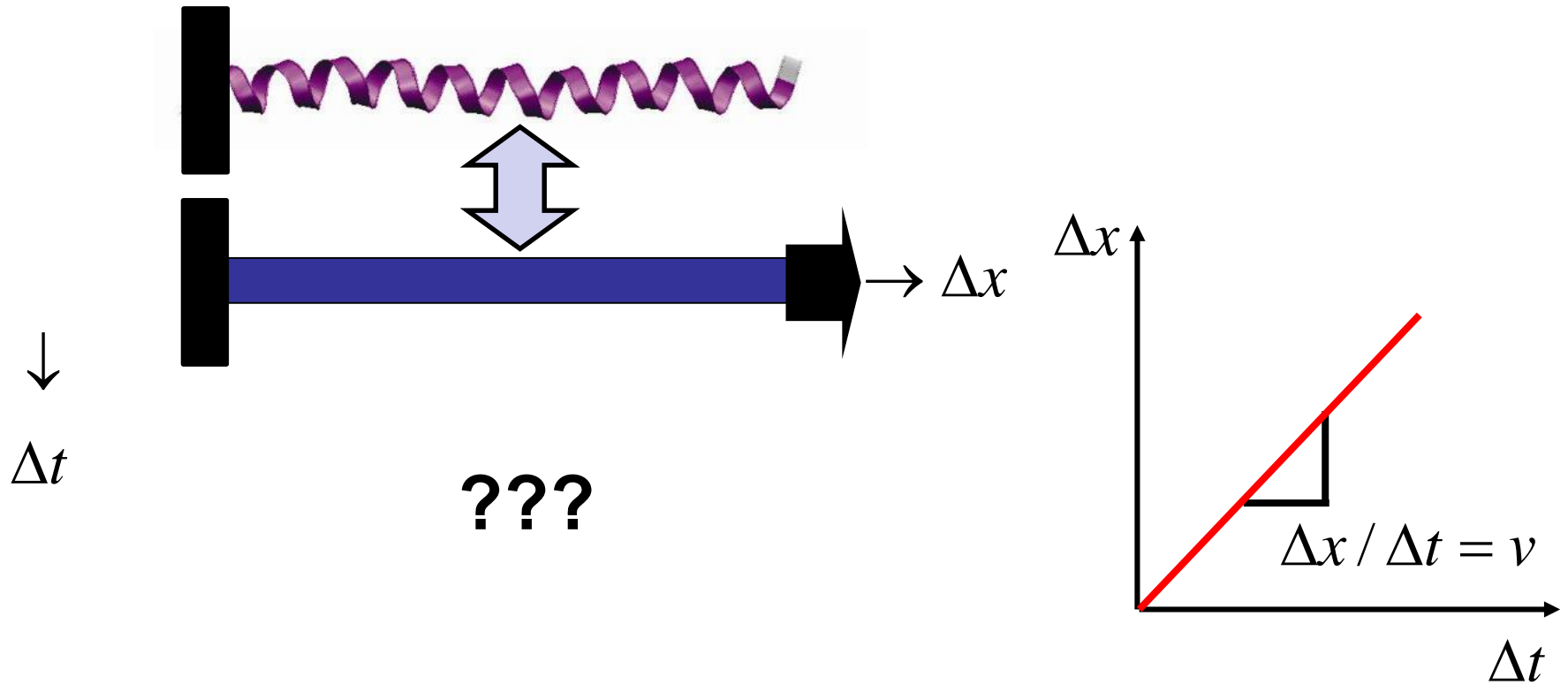
$$p = \exp\left(-\frac{E_b - f \cdot x_B}{k_B T} \right)$$

Off-rate = probability times vibrational frequency

$$\chi = \omega_0 \cdot p = \omega_0 \cdot \exp\left(-\frac{(E_b - f \cdot x_b)}{k_b \cdot T} \right) = \frac{1}{\tau} \qquad \omega_0 = 1 \times 10^{13} \; 1/\sec$$

$\tau = $ bond lifetime
(inverse of off-rate)[42]

Bell model

$$\Delta x / \Delta t = v$$
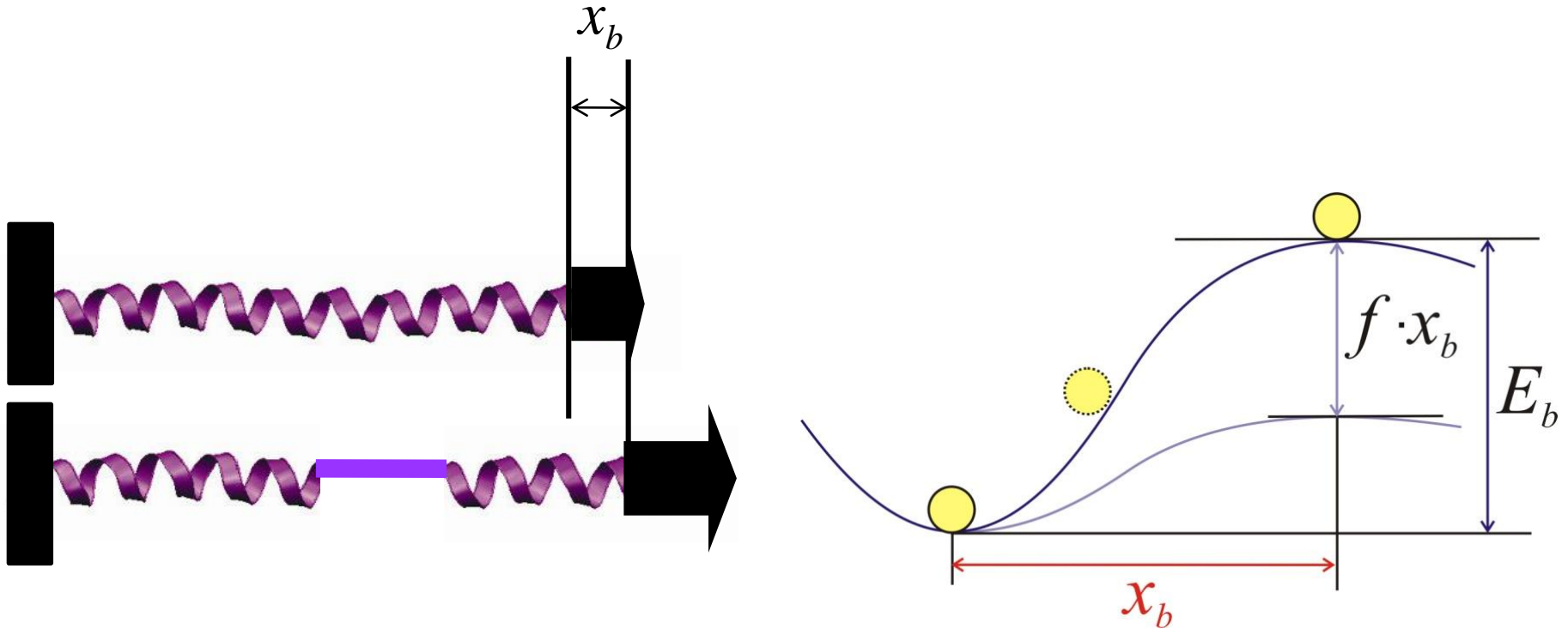
$$\Delta t$$

???

$$\Delta x / \Delta t = v \quad \text{pulling speed (at end of molecule)}$$

Bell model

broken turn

$$\Delta x / \Delta t = v$$
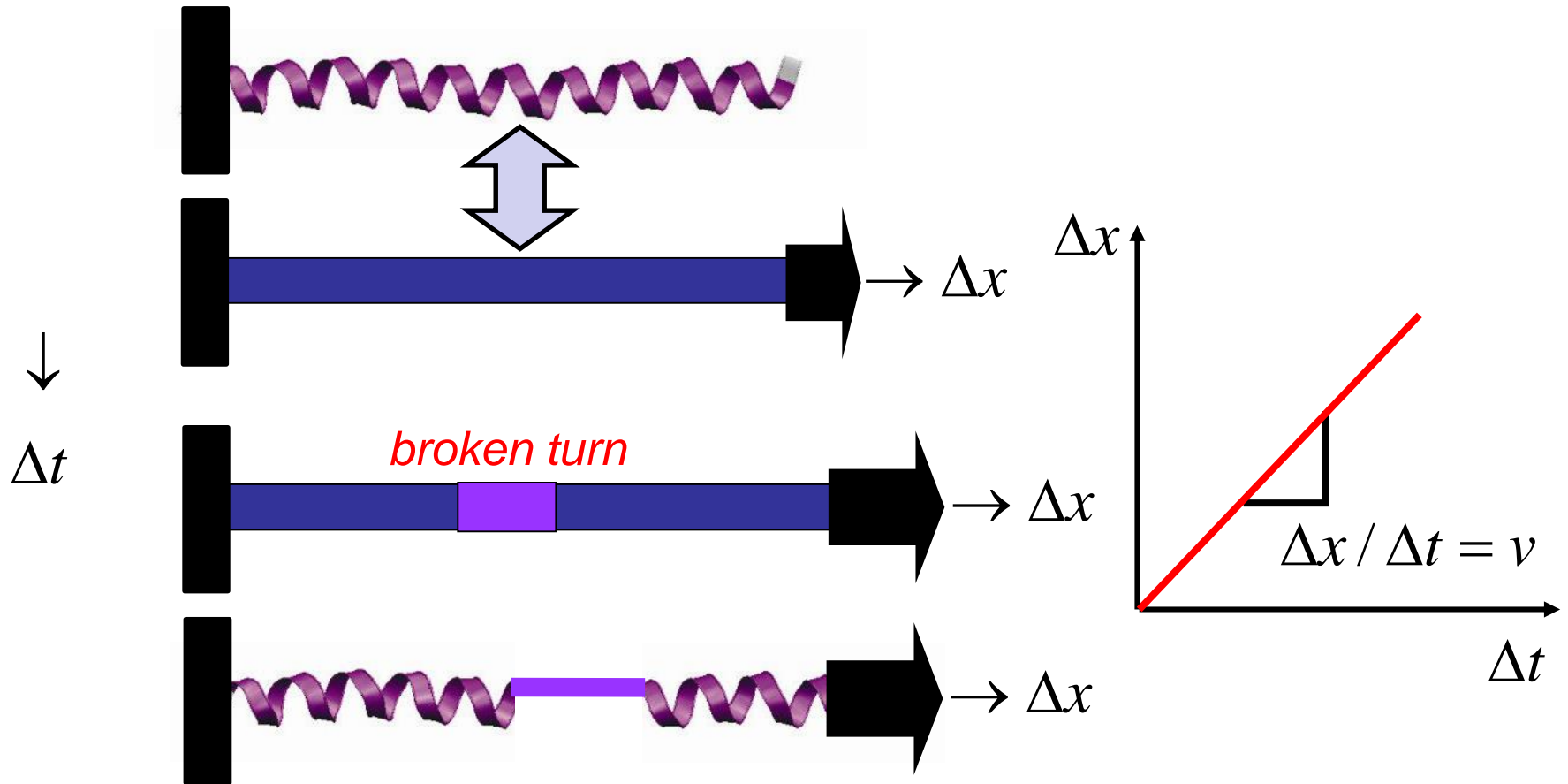
$$\Delta x / \Delta t = v \quad \text{pulling speed (at end of molecule)}$$

Structure-energy landscape link
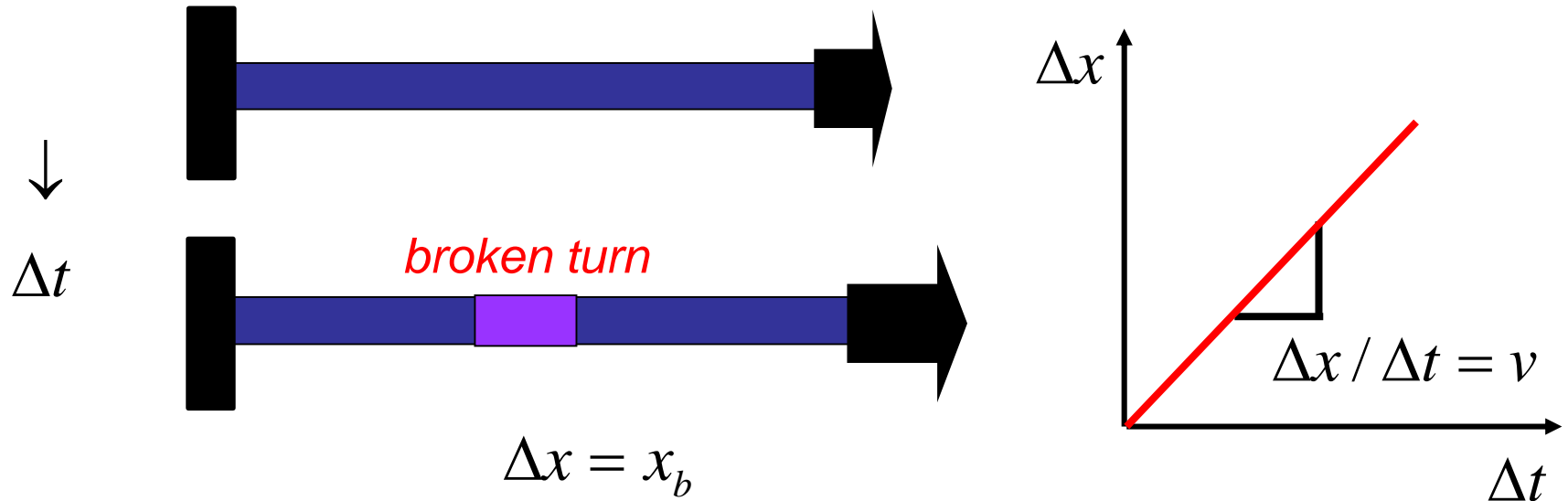

$$\Delta x = x_b$$

$$\Delta t = \tau \qquad \tau = \left[\omega_0 \cdot \exp\left(-\frac{(E_b - f \cdot x_b)}{k_b \cdot T} \right) \right]^{-1}$$

Bell model

Bond breaking at x_b (lateral applied displacement):

$$\chi \cdot x_b = \omega_0 \cdot \exp\left(-\frac{(E_b - f \cdot x_b)}{k_b \cdot T} \right) \cdot x_b = \Delta x / \Delta t = v$$

$$= 1 / \tau$$

pulling speed [46]

Bell model

$$\omega_0 \cdot \exp\left(- \frac{(E_b - f \cdot x_b)}{k_b \cdot T} \right) \cdot x_b = v$$

Solve this expression for f :

Bell model

$$\omega_0 \cdot \exp\left(-\frac{(E_b - f \cdot x_b)}{k_b \cdot T}\right) \cdot x_b = v$$

Solve this expression for f :

$$-\frac{(E_b - f \cdot x_b)}{k_b \cdot T} + \ln(\omega_0 \cdot x_b) = \ln v \quad \longleftarrow \quad \ln(..)$$

$$-E_b + f \cdot x_b = k_b \cdot T \big(\ln v - \ln(\omega_0 \cdot x_b)\big)$$

$$f = \frac{E_b + k_b \cdot T \big(\ln v - \ln(\omega_0 \cdot x_b)\big)}{x_b} = \frac{k_b \cdot T}{x_b}\ln v + \frac{k_b \cdot T}{x_b}\left(\frac{E_b}{k_b \cdot T} - \ln(\omega_0 \cdot x_b)\right)$$

$$f = \frac{k_b \cdot T}{x_b}\ln v - \frac{k_b \cdot T}{x_b}\left(\ln(\omega_0 \cdot x_b) - \frac{E_b}{k_b \cdot T}\right)$$

$$f = \frac{k_b \cdot T}{x_b}\ln v - \frac{k_b \cdot T}{x_b}\ln\left(\omega_0 \cdot x_b \cdot \exp\left(-\frac{E_b}{k_b \cdot T}\right)\right)$$

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Simplification by grouping of variables

Only system parameters, [distance/length]

$$f(v; x_b, E_b) = \frac{k_b \cdot T}{x_b} \cdot \ln v - \frac{k_b \cdot T}{x_b} \cdot \ln\left(\underbrace{\omega_0 \cdot x_b \cdot \exp\left(-\frac{E_b}{k_b \cdot T} \right)} \right)$$

$$=: v_0 = \omega_0 \cdot x_b \cdot \exp\left(-\frac{E_b}{k_b \cdot T} \right)$$

Bell model

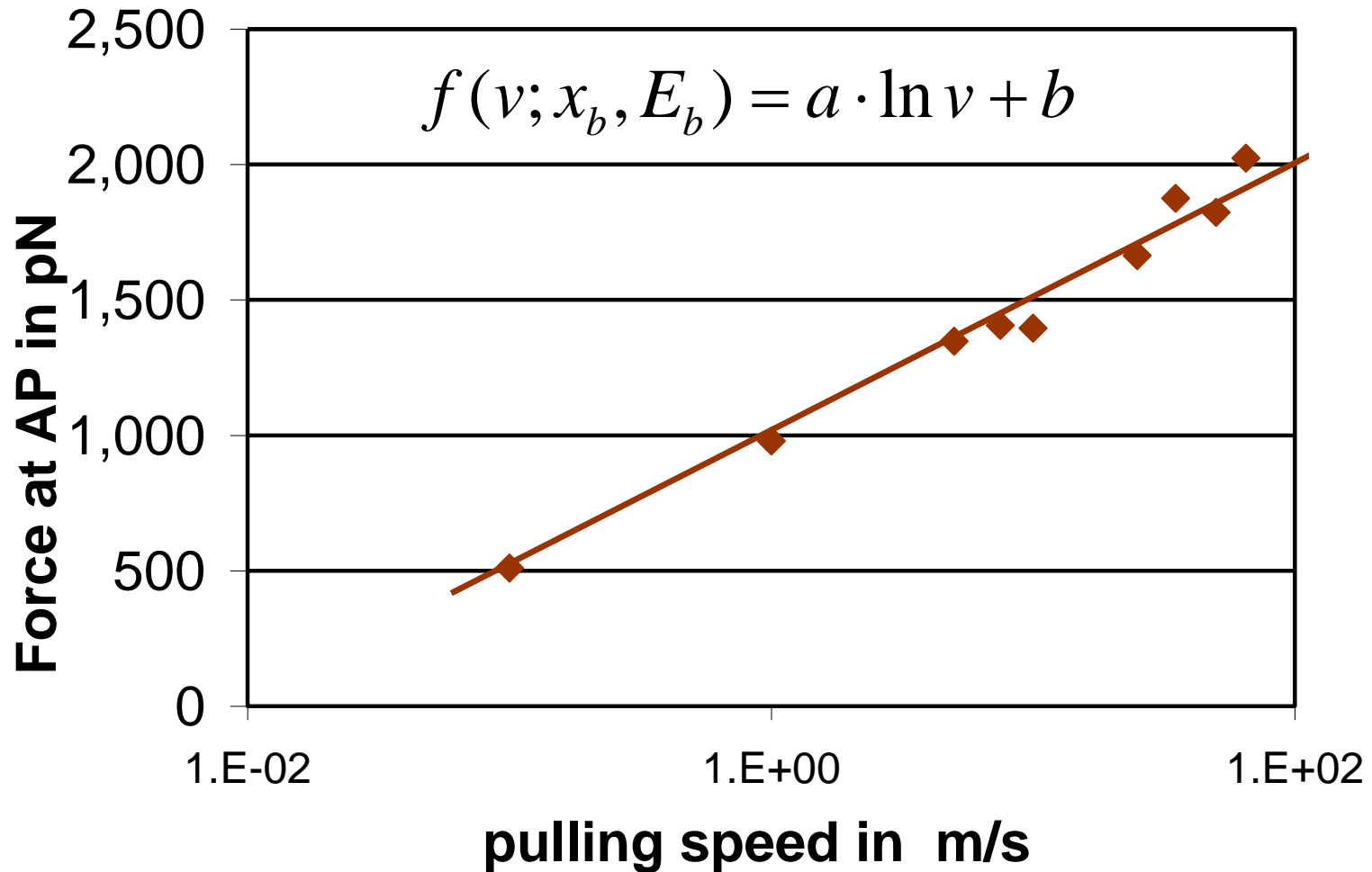$$\omega_0 \cdot \exp\left(-\frac{(E_b - f \cdot x_b)}{k_b \cdot T}\right) \cdot x_b = v$$

Results in:

$$f(v; x_b, E_b) = \frac{k_b \cdot T}{x_b} \cdot \ln v - \frac{k_b \cdot T}{x_b} \cdot \ln v_0 = \boxed{a \cdot \ln v + b}$$
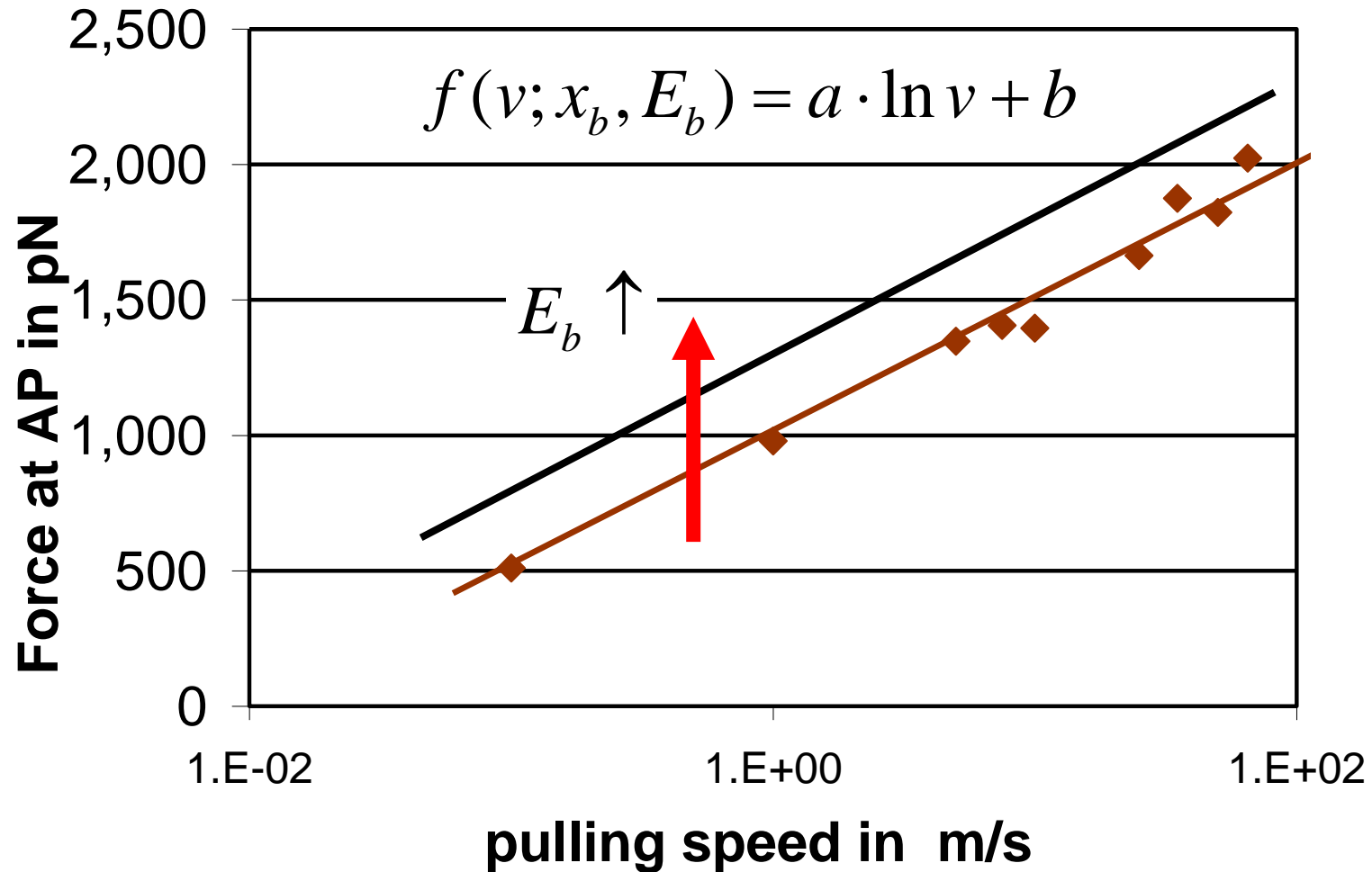
$$a = \frac{k_B \cdot T}{x_b}$$

$$b = -\frac{k_B \cdot T}{x_b} \cdot \ln v_0$$

$f \sim \ln v$ behavior of strength

$$f(v; x_b, E_b) = a \cdot \ln v + b$$

Force at AP in pN (y-axis): 0, 500, 1,000, 1,500, 2,000, 2,500
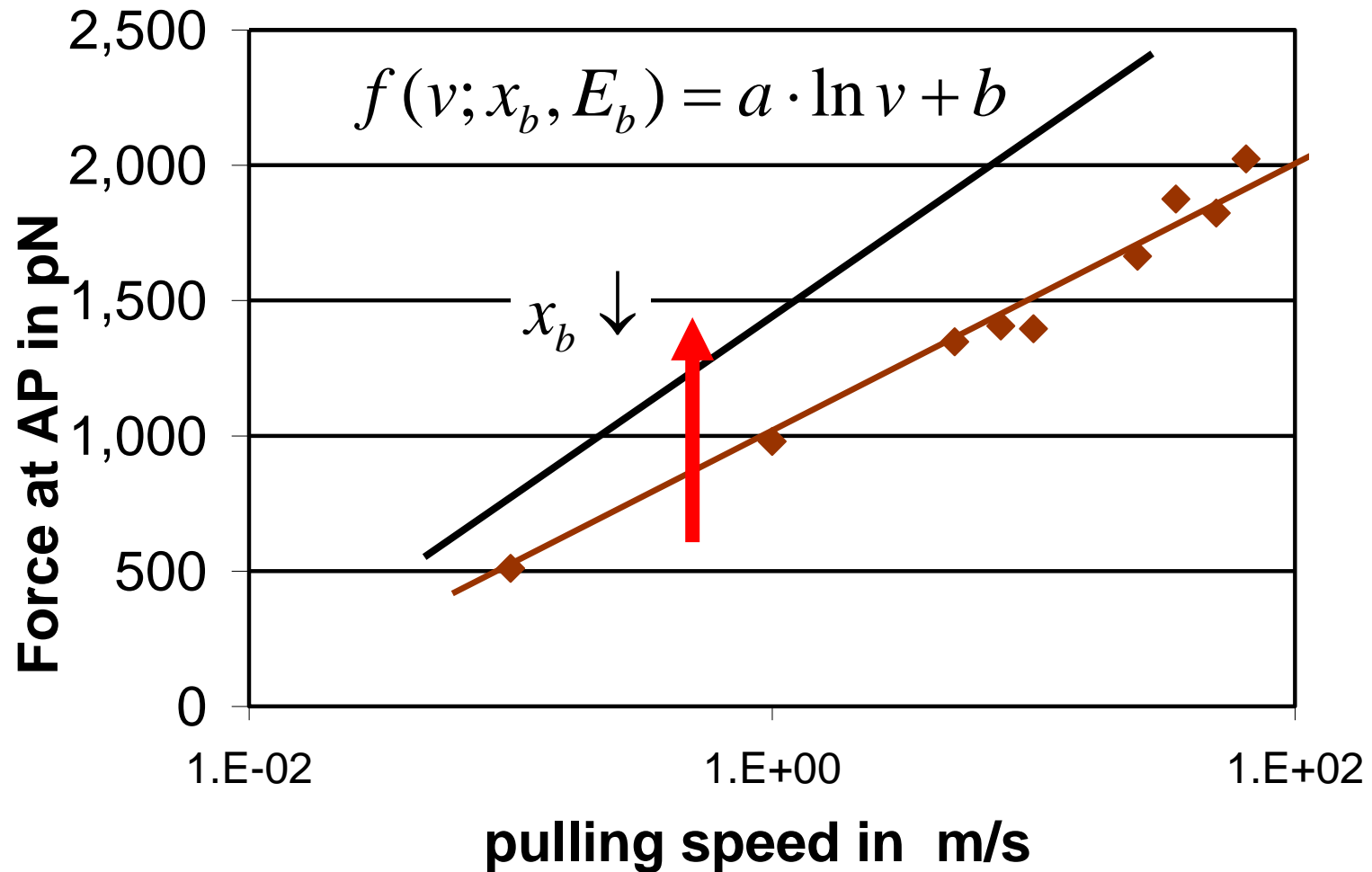
pulling speed in m/s (x-axis): 1.E-02, 1.E+00, 1.E+02

E_b= 5.6 kcal/mol and x_b= 0.17 Å (results obtained from fitting to the simulation data)

Scaling with E_b : shifts curve

$$f(v; x_b, E_b) = a \cdot \ln v + b$$
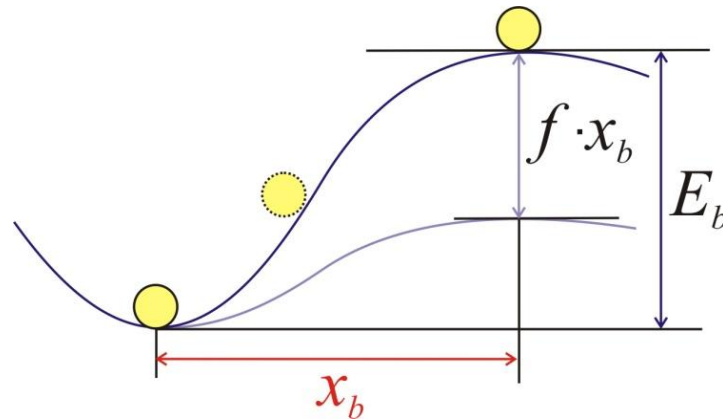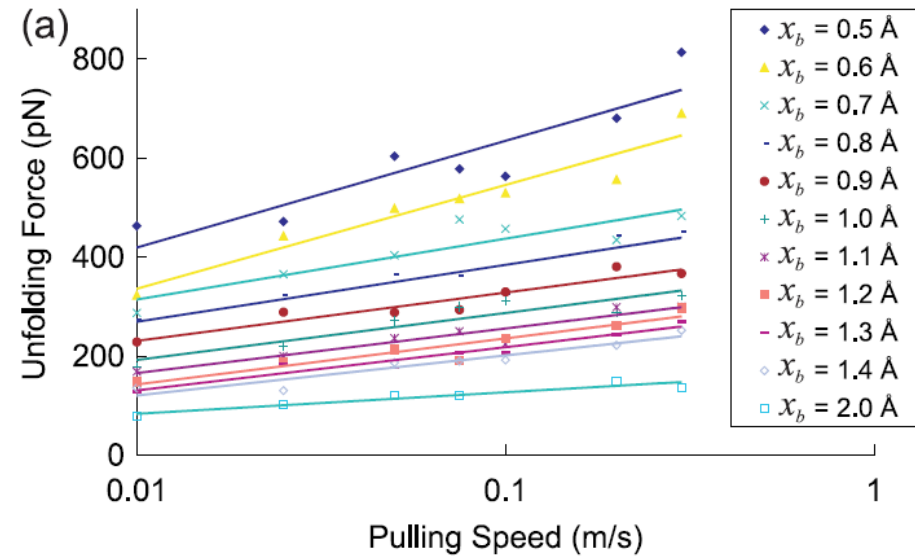
E_b ↑

Force at AP in pN

pulling speed in m/s

$$a = \frac{k_B \cdot T}{x_b} \qquad b = -\frac{k_B \cdot T}{x_b} \cdot \ln v_0 \qquad v_0 = \omega_0 \cdot x_b \cdot \exp\left(-\frac{E_b}{k_b \cdot T}\right)$$

Scaling with x_b: changes slope

$$f(v; x_b, E_b) = a \cdot \ln v + b$$

Force at AP in pN

2,500

2,000

1,500

x_b ↓

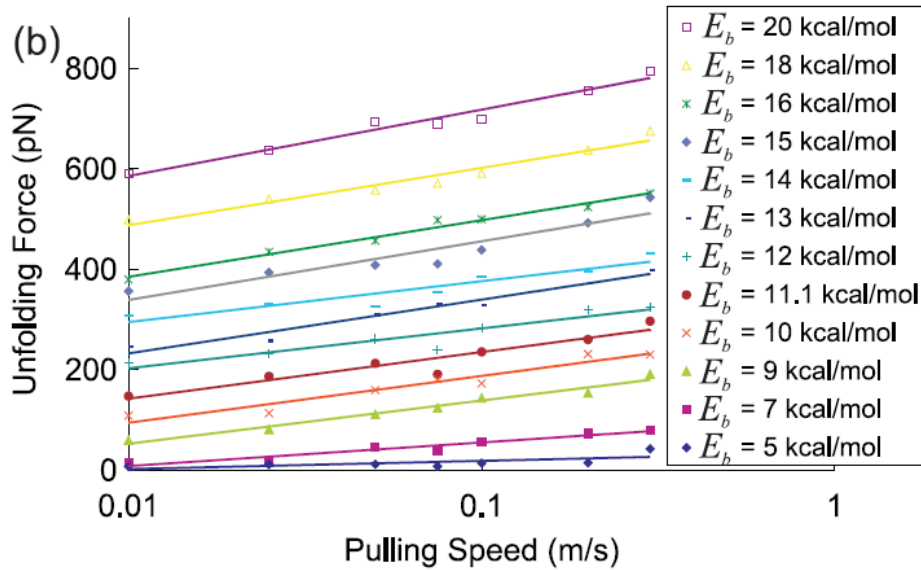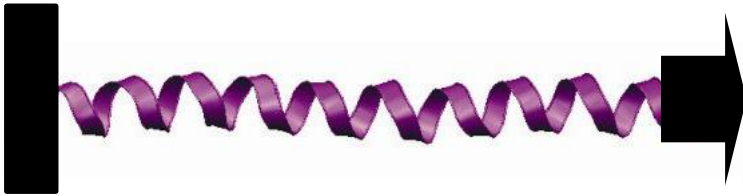1,000

500

0

1.E-02 1.E+00 1.E+02

pulling speed in m/s

$$a = \frac{k_B \cdot T}{x_b} \qquad b = -\frac{k_B \cdot T}{x_b} \cdot \ln v_0 \qquad v_0 = \omega_0 \cdot x_b \cdot \exp\left(-\frac{E_b}{k_b{}^{53} \cdot T}\right)$$

Simulation results

Bertaud, Hester, Jimenez, and Buehler, *J. Phys. Cond. Matt.,* 2010

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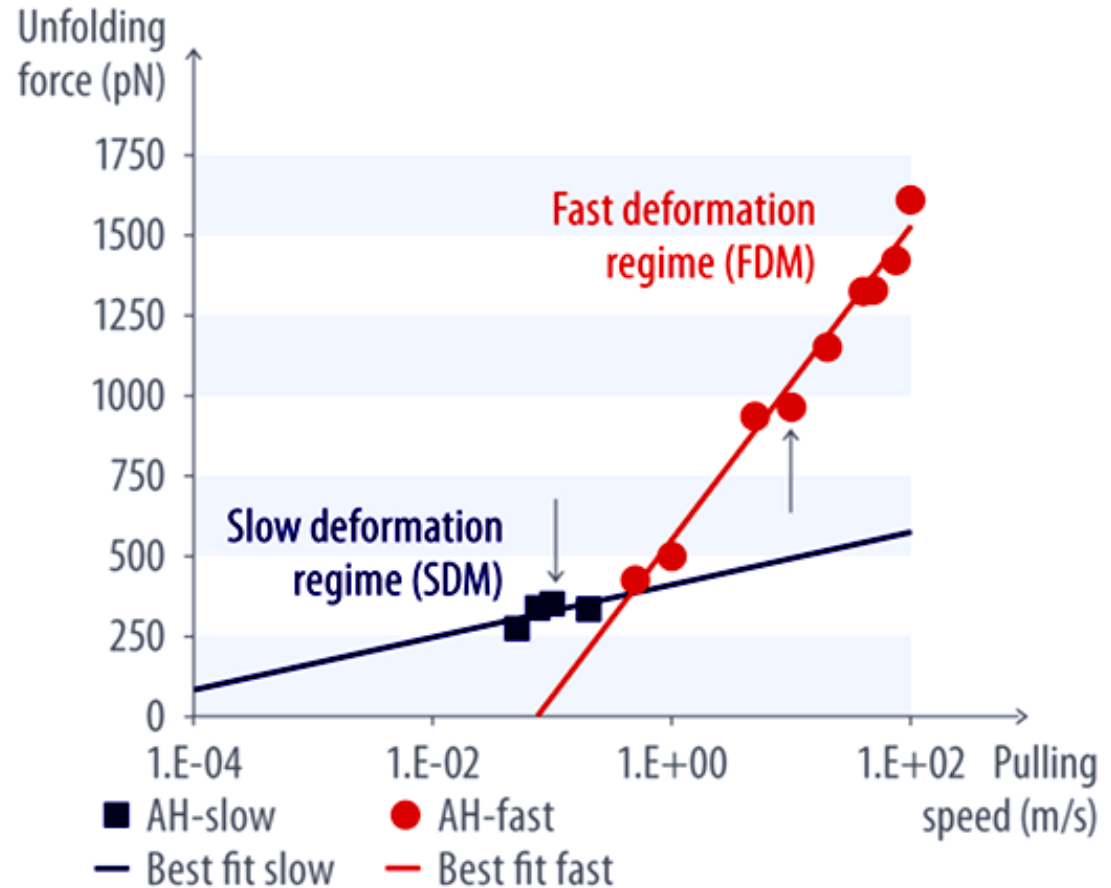# *Mechanisms associated with protein fracture*

Change in fracture mechanism

Single AH structure

FDM: Sequential
HB breaking

SDM: Concurrent
HB breaking
(3..5 HBs)

Simulation span: 250 ns
Reaches deformation speed O(cm/sec)

Ackbarow, Chen, *et al.*, *Proc. Nat'l Academy of Sciences USA*, 2007

Analysis of energy landscape parameters

Table 1. Summary of the differences between the SDM and FDM, for AH1, AH2, and BS

| Parameter	AH1 (AH2) domain		BS domain	
	SDM	FDM	SDM	FDM
Pulling speed, m/s	$v < 0.4$ (4)	$v > 0.4$ (4)	$v < 10$	$v > 10$
Unfolding force, pN	$F < 350$ (400)	$F > 350$ (400)	$F < 4,800$	$F > 4,800$
E_b, kcal/mol	11.1 (9.11)	4.87 (3.08)	11.08	1.82
x_b, Å	1.2 (1.19)	0.2 (0.11)	0.138	0.019
HB-breaking mechanism	Simultaneous	Sequential	Simultaneous	Sequential

The values in parentheses in the AH columns represent the results for AH2.

Energy single H-bond: ≈3-4 kcal/mol

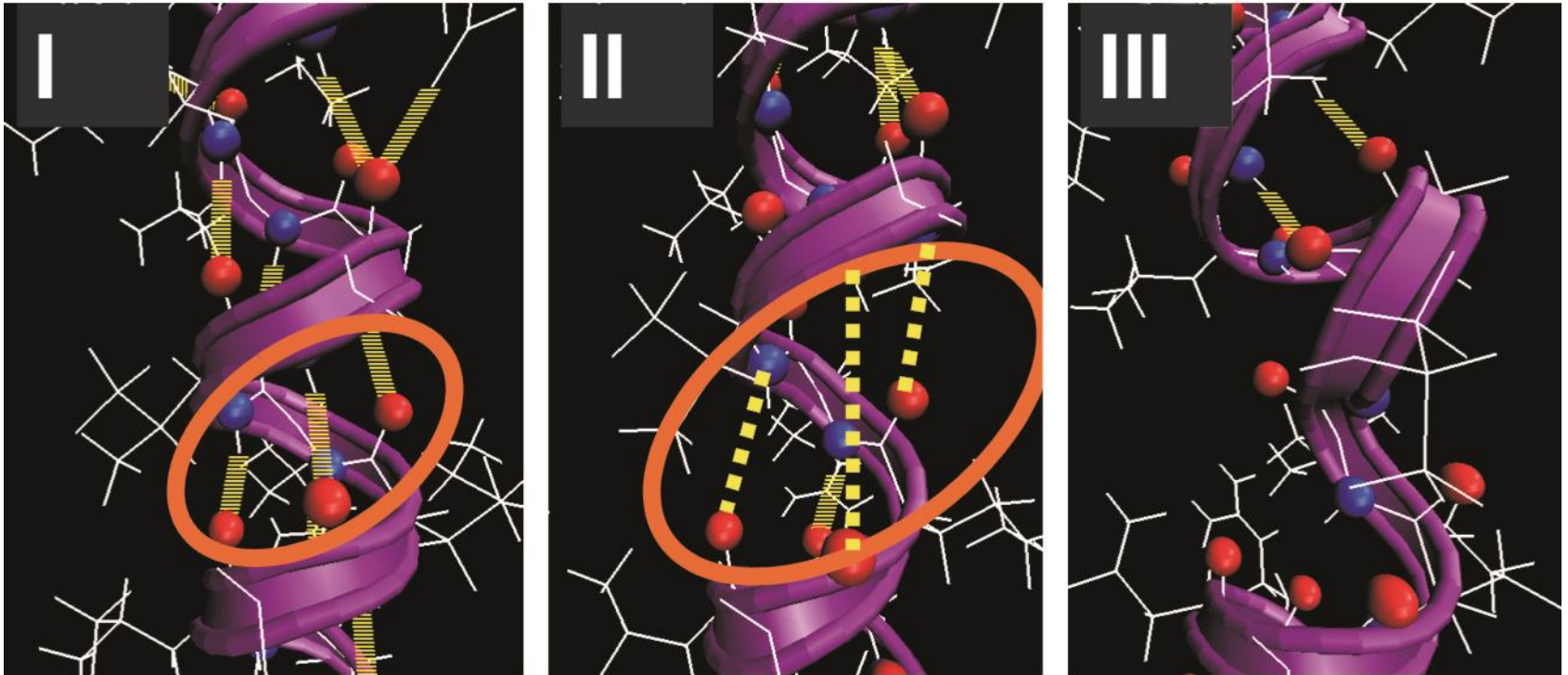*What does this mean???*

Ackbarow, Chen, *et al*., *Proc. Nat'l Academy of Sciences USA*, 2007
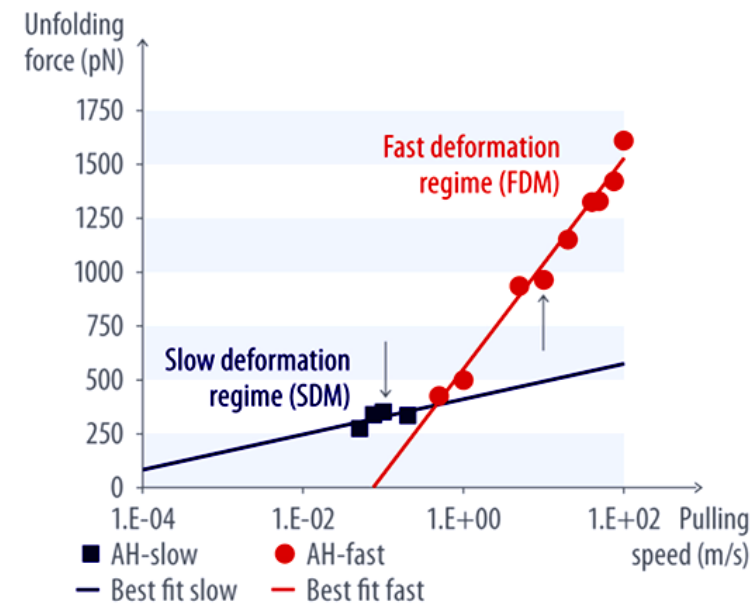
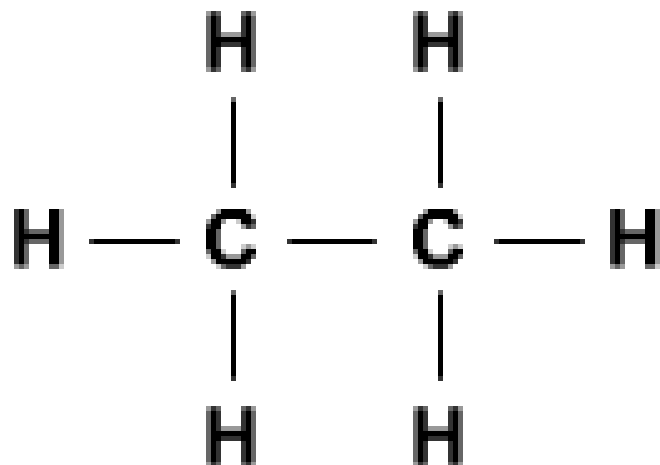# H-bond rupture dynamics: mechanism
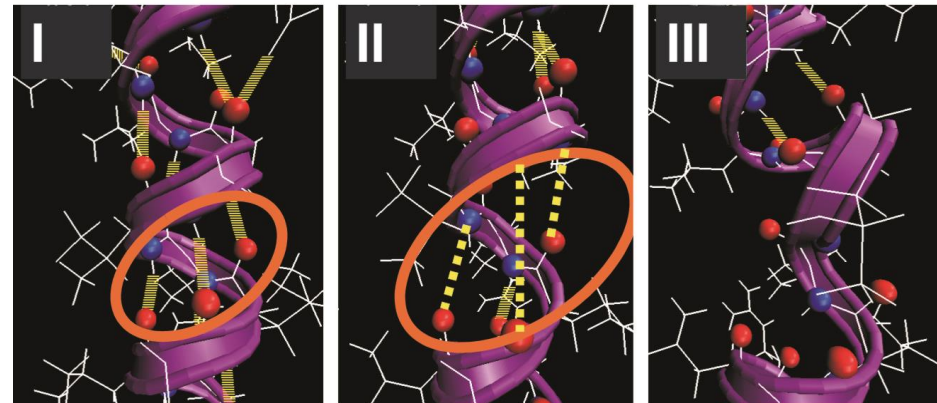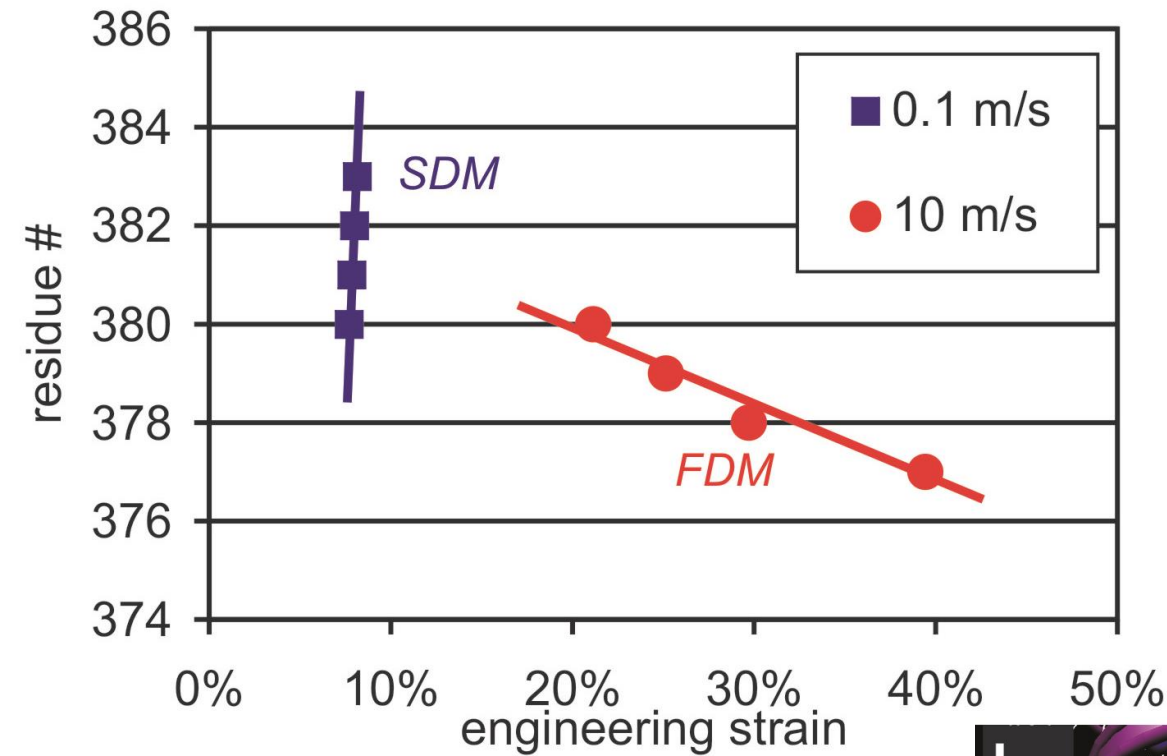
H-bond rupture dynamics: mechanism

I: All HBs are intact

II: Rupture of 3 HBs – simultaneously; **within $\tau \approx$ 20 ps**

III: Rest of the AH relaxes – slower deformation…

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Ackbarow, Chen, *et al*., *Proc. Nat'l Academy of Sciences USA*, 2007

3. Reactive force fields

Are all bonds the same? - valency in hydrocarbons

Ethane C_2H_6
(stable configuration)
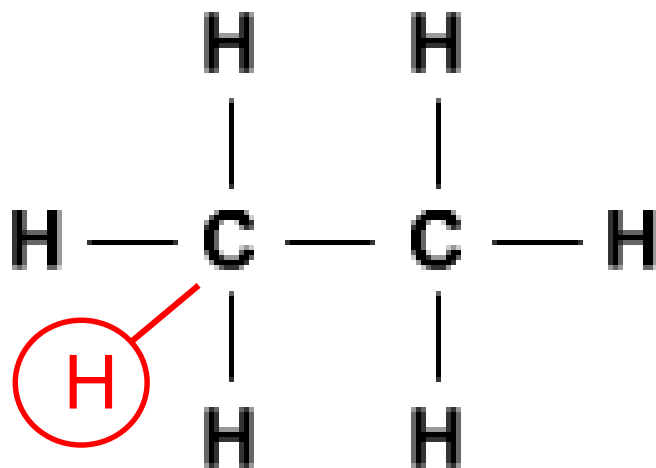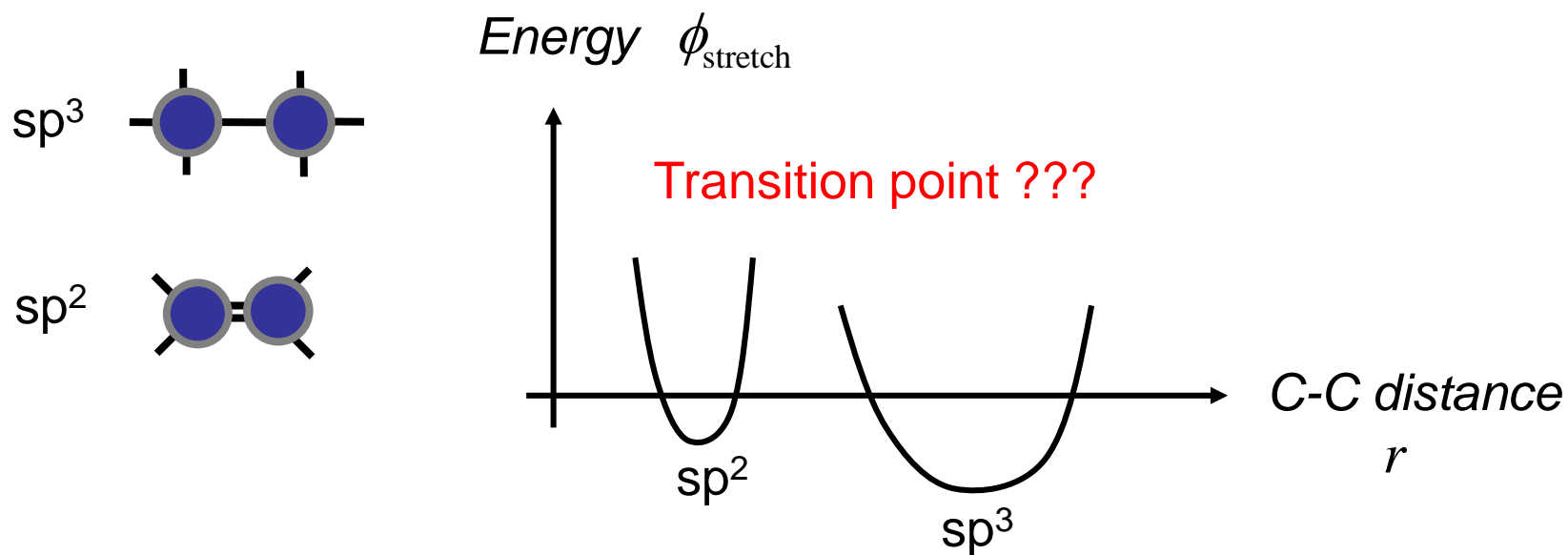
All bonds are not the same!

Adding another H is not favored

Diversity of types of chemical bonds

- **Primary bonds ("strong")**
  - Ionic (ceramics, quartz, feldspar - **rocks**)
  - Covalent (**silicon**)
  - Metallic (copper, nickel, **gold**, silver)
    (high melting point, 1000-5,000K)

- **Secondary bonds ("weak")**
  - Van der Waals (**wax**, low melting point)
  - Hydrogen bonds (proteins, **spider silk**)
    (melting point 100-500K)

- Ionic: Non-directional (point charges interacting)
- Covalent: Directional (bond angles, torsions matter)
- Metallic: Non-directional (electron gas concept)

Difference of material properties originates from different atomic interactions

Challenge: chemical reactions

sp^3

sp^2

Energy ϕ_{stretch}

Transition point ???

sp^2

sp^3

C-C distance r

Two harmonic potential scan not describe chemical reactions

Why can not model chemical reactions with CHARMM-like potentials?

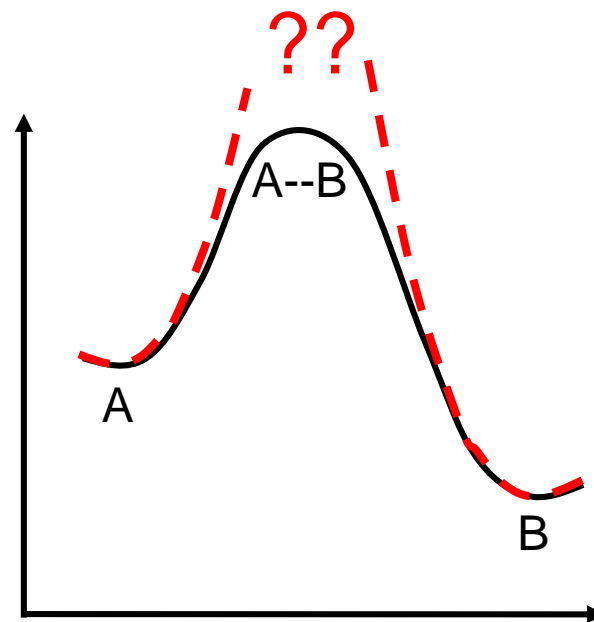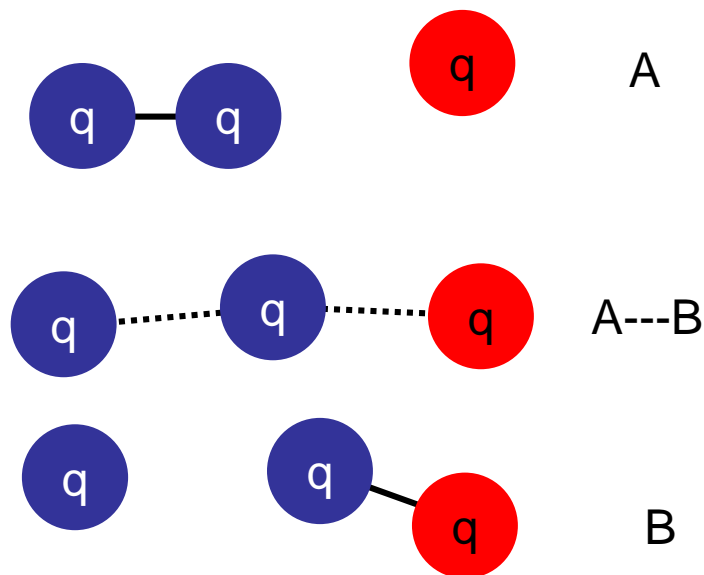$$\phi_{\text{stretch}} = \frac{1}{2} k_{\text{stretch}} (r - r_0)^2$$

Set of parameters only valid for particular molecule type / type of chemical bond

$$\phi_{\text{bend}} = \frac{1}{2} k_{\text{bend}} (\theta - \theta_0)^2$$

$$k_{\text{stretch},sp^2} \neq k_{\text{stretch},sp^3}$$

Reactive potentials or reactive force fields *overcome these limitations*

Key features of reactive potentials

- How can one accurately describe the transition energies during chemical reactions?

- Use computationally more efficient descriptions than relying on purely quantum mechanical (QM) methods (see part II, **methods limited to 100 atoms**)

$$H - C \equiv C - H \xrightarrow{+H_2} H_2 - C = C - H_2$$

involves processes with electrons

A

A---B

B

??

A--B

A

B

Overview: potential energy models

- **Empirical models: mathematical functions with parameters (fitted to experiment or quantum mechanics)**
  - Pair potentials (LJ, Morse, Buck., harmonic)
  - Embedded atom models/effective medium theories
  - Multi-body potentials (e.g. Tersoff, CHARMM, etc.)
  - Reactive potentials (ReaxFF)

- Semi-empirical models (explicitly note electronic structure)
  - Tight binding
  - MINDO (=Modified Intermediate Neglect of Differential Overlap), NINDO (=Intermediate Neglect of Differential Overlap)

- Quantum mechanical models: Start from Schroedinger's equation (and make approximations to be able to solve it)
  - Quantum chemistry (Hartree-Fock)
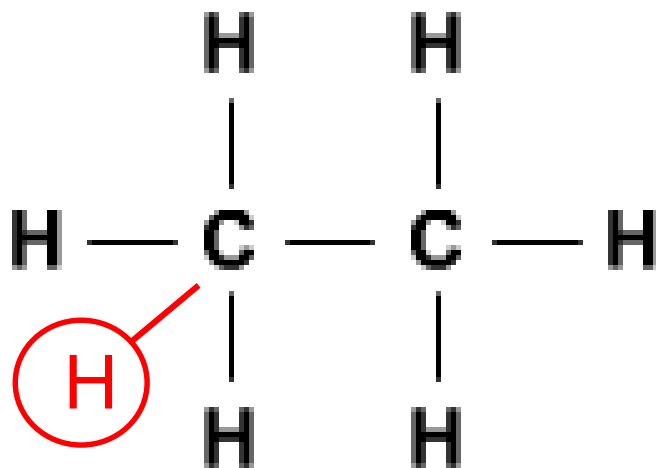 - Density Functional Theory
  - Quantum Monte Carlo

Energy only (and positions, velocities etc.)

Energy and electronic structure

Computational efficiency

Increased accuracy & "**transferability**"

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After: G. Ceder

Are all bonds the same? - valency in hydrocarbons

Ethane C_2H_6
(stable configuration)

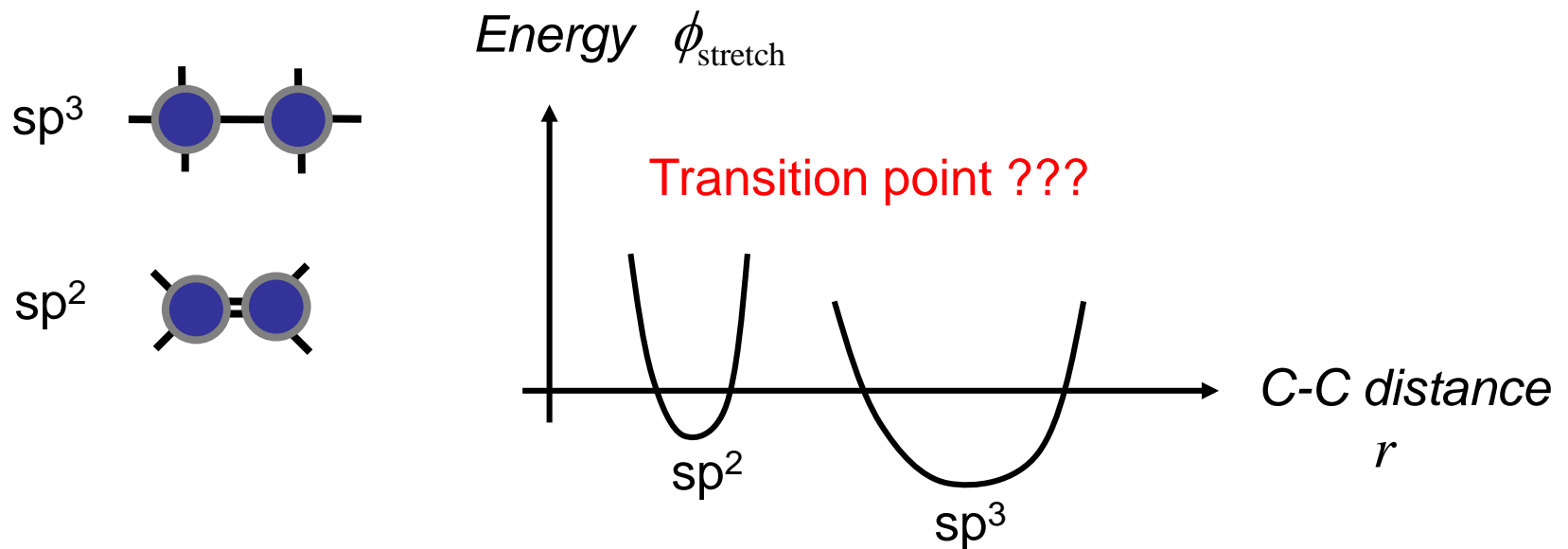*All bonds are not the same!*

Adding another H is not favored

67

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      (high melting point, 1000-5,000K)

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Difference of material properties originates from different atomic interactions

Challenge: chemical reactions

sp^3

sp^2

Energy ϕ_{stretch}

Transition point ???

sp^2

sp^3

C-C distance
r

Two harmonic potential scan not describe chemical reactions

Why can not model chemical reactions with CHARMM-like potentials?

$$\phi_{\text{stretch}} = \frac{1}{2} k_{\text{stretch}} (r - r_0)^2$$

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Reactive potentials or reactive force fields *overcome these limitations*

Key features of reactive potentials

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- Use computationally more efficient descriptions than relying on purely quantum mechanical (QM) methods (see part II, **methods limited to 100 atoms**)

$$H-C \equiv C-H \xrightarrow{+H_2} H_2-C=C-H_2$$

involves processes with electrons
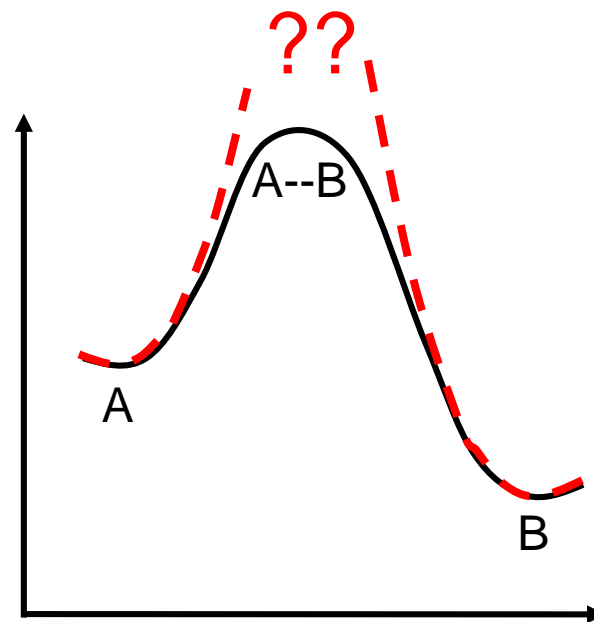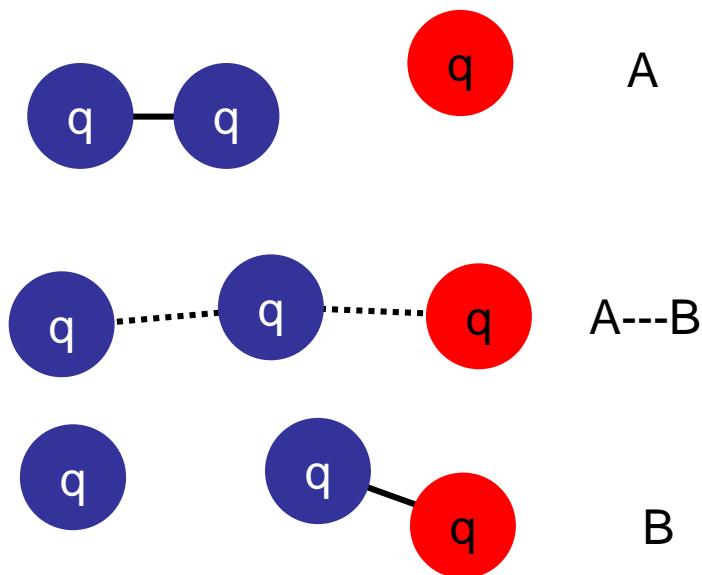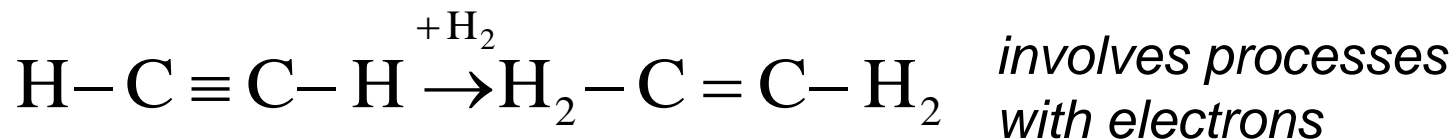
Key features of reactive potentials

- Molecular model that is capable of describing **chemical reactions**

- **Continuous energy landscape during reactions** (key to enable integration of equations)

- No typing necessary, that is, atoms can be sp, sp2, sp3… w/o further "tags" – **only element types**

- **Computationally efficient** (that is, should involve finite range interactions), so that large systems can be treated (> 10,000 atoms)

- **Parameters with physical meaning** (such as for the LJ potential)

Theoretical basis: bond order potential

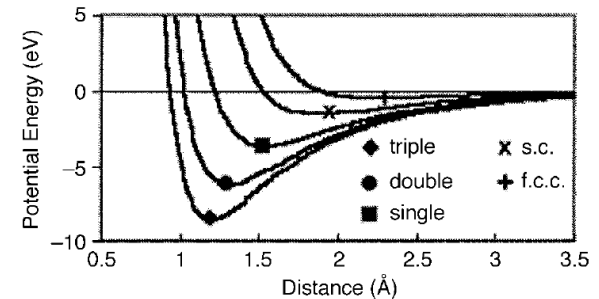**Concept:** Use pair potential that depends on atomic environment

$$\phi(r_{ij}) = \phi_{\mathrm{R}}\left(r_{ij}\right) - M_{ij}\phi_A(r_{ij})$$

$$M_{ij} \sim Z^{-\delta}$$

Modulate strength of
attractive part
(e.g. by coordination,
or "bond order")

Abell, Tersoff

$$k(r) \sim k_0 M_{ij}(Z, \delta)$$

Changes in spring constant as function of bond order
Continuous change possible
= **continuous energy landscape during chemical reactions**

Theoretical basis: bond order potential

Concept: Use pair potential that depends on atomic environment

Recall $\phi(r_{ij}) = 4\varepsilon\left[\left(\dfrac{\sigma}{r_{ij}}\right)^{12} - \left(\dfrac{\sigma}{r_{ij}}\right)^{6}\right]$

$\phi(r_{ij}) = \phi_{\mathrm{R}}(r_{ij}) - M_{ij}\phi_A(r_{ij})$

$\downarrow$

$M_{ij} \sim Z^{-\delta}$

Modulate strength of attractive part (e.g. by coordination, or "bond order")

$\phi(r_{ij}) = 4\varepsilon\left[\left(\dfrac{\sigma}{r_{ij}}\right)^{12} - M_{ij}\left(\dfrac{\sigma}{r_{ij}}\right)^{6}\right]$

Abell, Tersoff

$k(r) \sim k_0 M_{ij}(Z,\delta)$
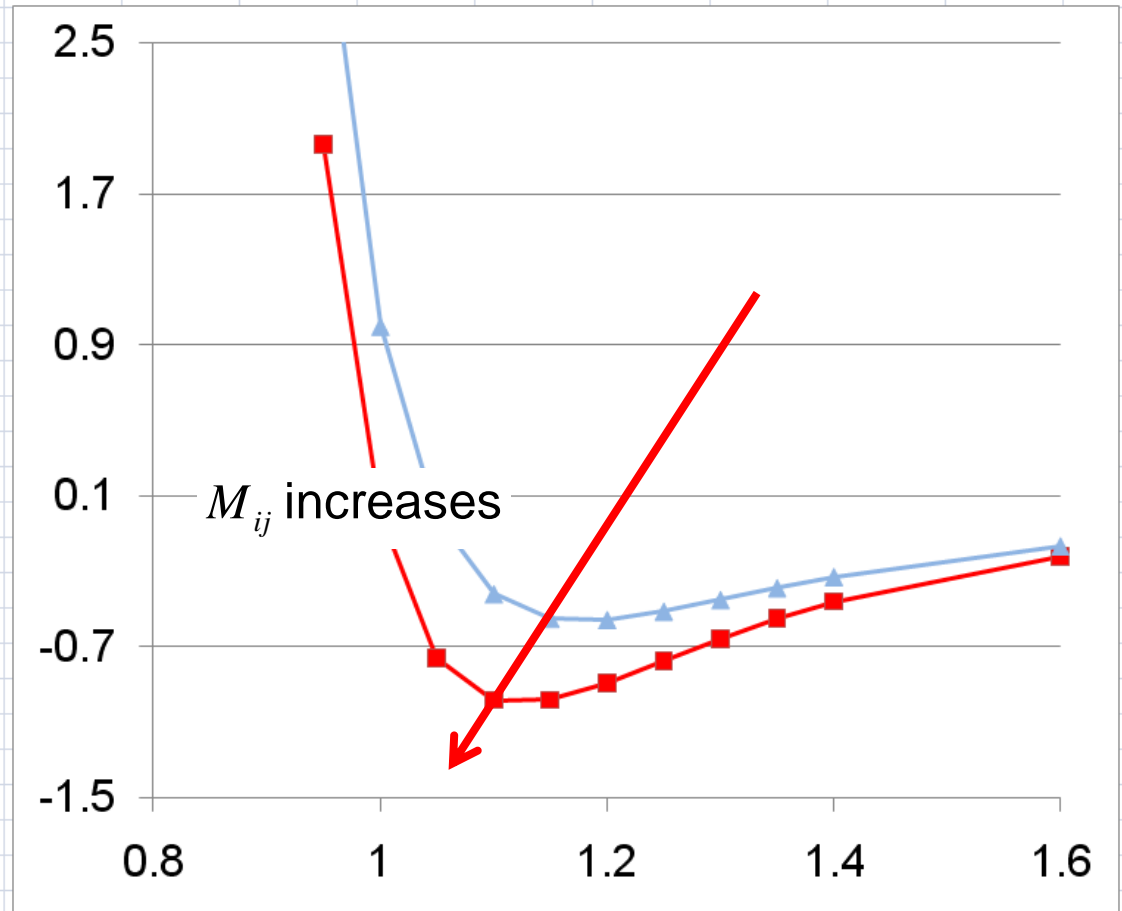
Changes in spring constant as function of bond order
Continuous change possible

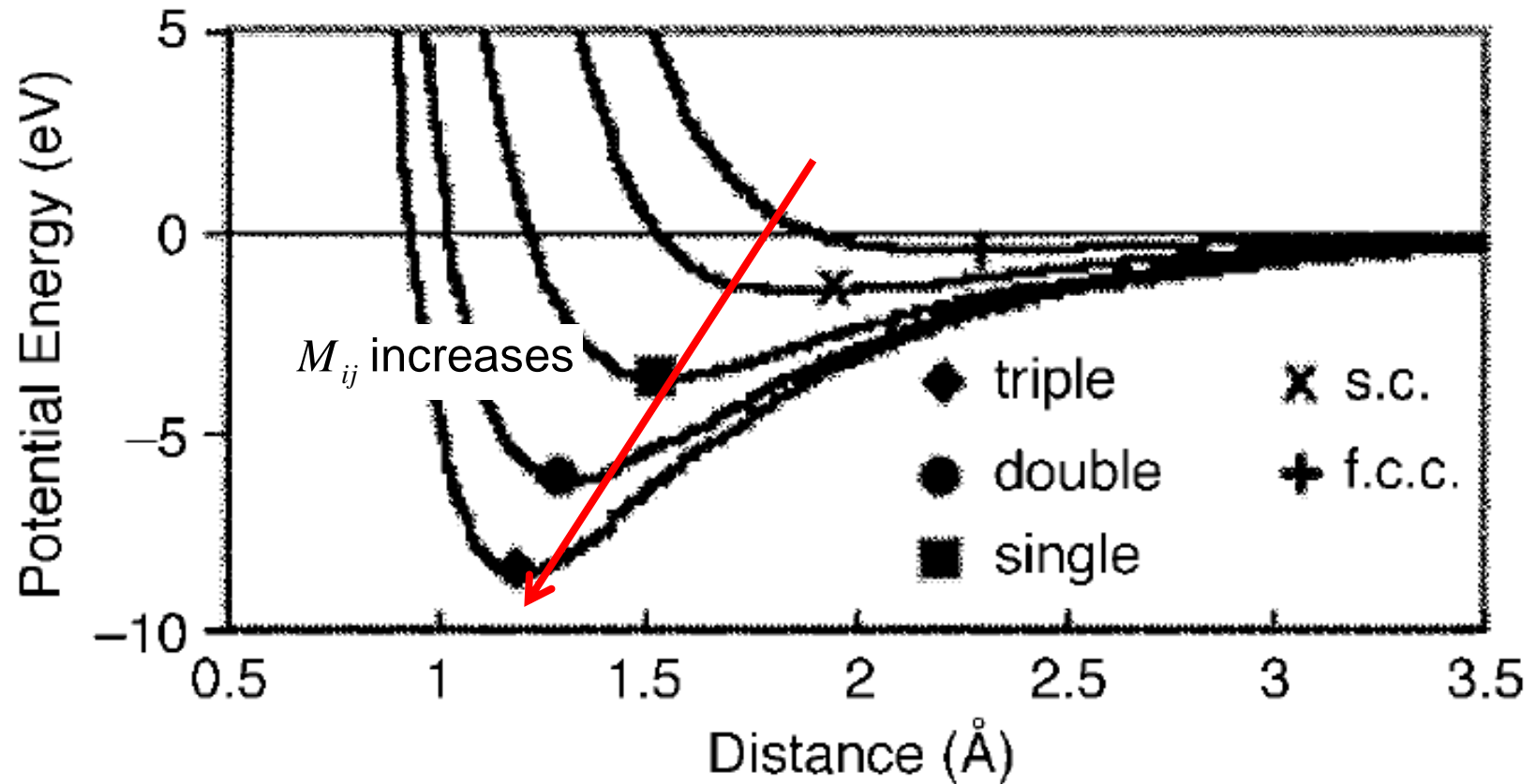**= continuous energy landscape during chemical reactions**

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Example – Excel worksheet

LJ potential with bond order term

ε	1	ε	1
σ	1	σ	1
M(BO)	1	M(BO)	0.75

0.95	1.960975	0.95	3.321349
1	0	1	1
1.05	-0.75751	1.05	-0.0113
1.1	-0.98337	1.1	-0.4189
1.15	-0.98168	1.15	-0.54935
1.2	-0.89097	1.2	-0.55607
1.25	-0.7737	1.25	-0.51155
1.3	-0.65702	1.3	-0.44984
1.35	-0.55162	1.35	-0.38643
1.4	-0.46069	1.4	-0.32788
1.6	-0.22421	1.6	-0.1646
1.8	-0.11415	1.8	-0.08475
2	-0.06152	2	-0.0459
2.2	-0.03497	2.2	-0.02615
2.5	-0.01632	2.5	-0.01222
3	-0.00548	3	-0.00411

$$\phi(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - M_{ij}\left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$
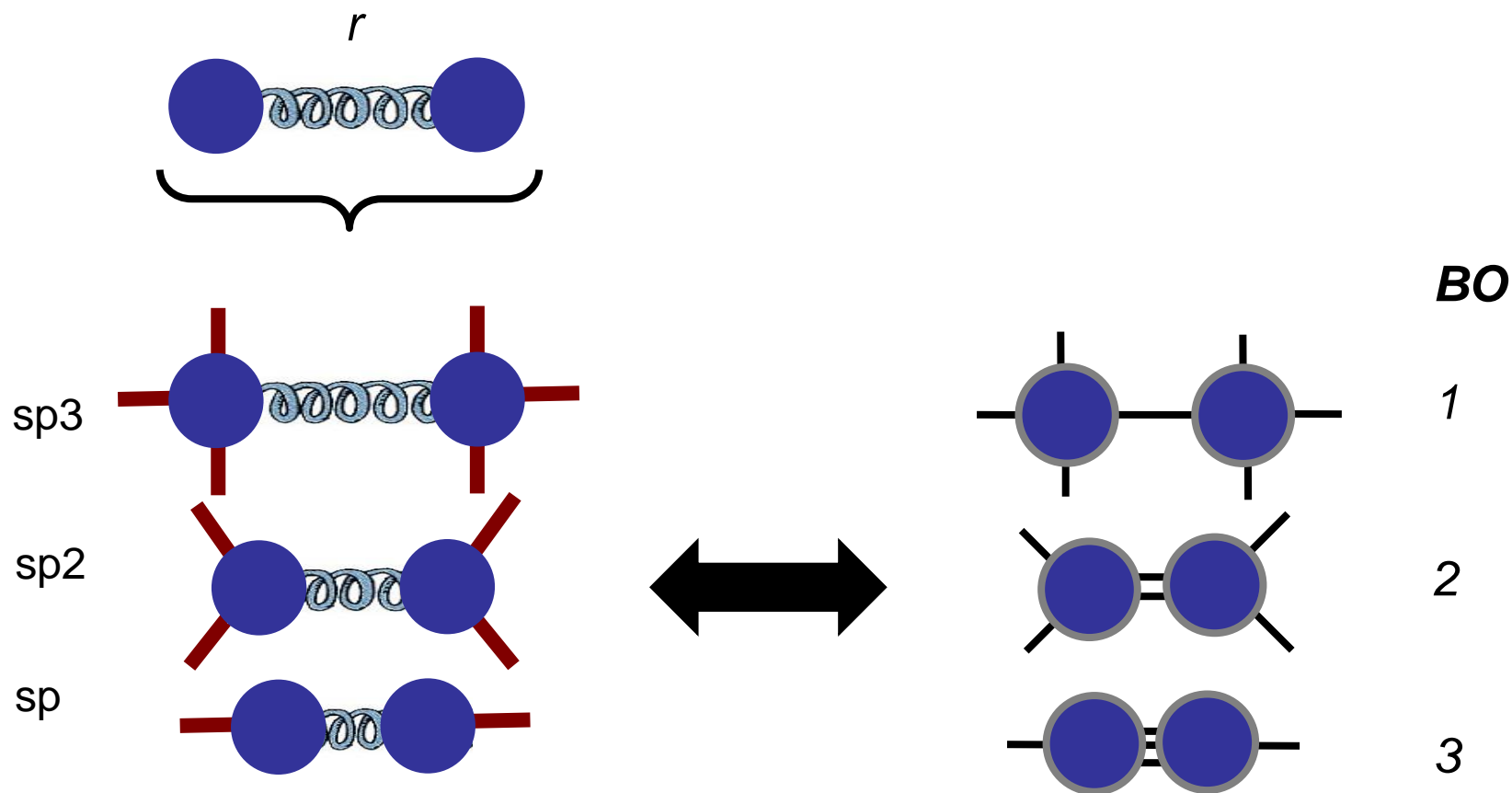
M_{ij} increases

Excel file posted on Stellar
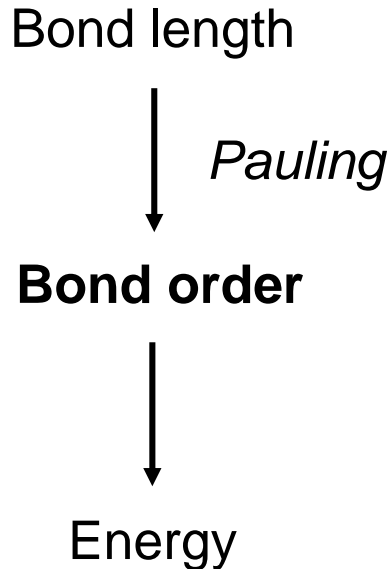
Theoretical basis: bond order potential

Effective pair-interactions for various C-C (carbon) bonds

D. Brenner, 2000

Concept of bond order (BO)

Bond order based energy landscape

Bond length

Pauling

Bond order

Energy

Bond order potential
Allows for a more general
description of chemistry
All energy terms dependent
***on bond order***

Bond length
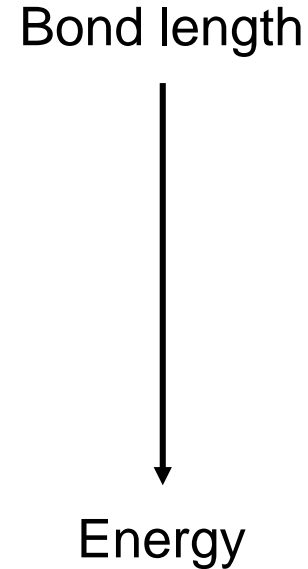
Energy

Conventional potential
(e.g. LJ, Morse)

Historical perspective of reactive bond order potentials

- 1985: Abell: General expression for binding energy as a sum of near nieghbor pair interactions moderated by local atomic environment

- 1990s: Tersoff, Brenner: Use Abell formalism applied to silicon (successful for various solid state structures)

- 2000: Stuart et al.: Reactive potential for hydrocarbons

- 2001: Duin, Godddard et al.: Reactive potential for hydrocarbons "ReaxFF"

- 2002: Brenner et al.: Second generation "REBO" potential for hydrocarbons

- 2003-2005: Extension of ReaxFF to various materials including metals, ceramics, silicon, polymers and more in Goddard's group

Example: ReaxFF reactive force field
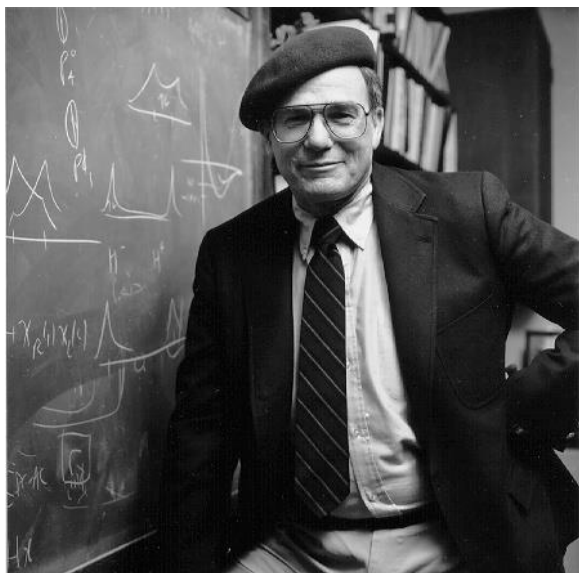
William A. Goddard III
California Institute of Technology

Adri C.T. v. Duin
California Institute of Technology

ReaxFF: A Reactive Force Field for Hydrocarbons

Adri C. T. van Duin,[†,∥] Siddharth Dasgupta,[‡] Francois Lorant,[§] and William A. Goddard III[*,‡]

Department of Fossil Fuels and Environmental Geochemistry, Drummond Building, University of Newcastle, Newcastle upon Tyne NE1 7RU, United Kingdom, Materials and Process Simulation Center, Beckman Institute (139-74), Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, and Institut Français du Pètrole, Geology and Geochemistry Research Division, 1-4 Avenue de Bois-Preau, 92852 Rueil-Malmaison, France

To make practical the molecular dynamics simulation of large scale reactive chemical systems (1000s of atoms), we developed ReaxFF, a force field for reactive systems. ReaxFF uses a general relationship between bond distance and bond order on one hand and between bond order and bond energy on the other hand that leads to proper dissociation of bonds to separated atoms. Other valence terms present in the force field (angle and torsion) are defined in terms of the same bond orders so that all these terms go to zero smoothly as bonds break. In addition, ReaxFF has Coulomb and Morse (van der Waals) potentials to describe nonbond interactions between all atoms (no exclusions). These nonbond interactions are shielded at short range so that the Coulomb and van der Waals interactions become constant as $R_{ij} \rightarrow 0$. We report here the ReaxFF for hydrocarbons. The parameters were derived from quantum chemical calculations on bond dissociation and reactions of small molecules plus heat of formation and geometry data for a number of stable hydrocarbon compounds. We find that the ReaxFF provides a good description of these data. Generally, the results are of an accuracy similar or better than PM3, while ReaxFF is about 100 times faster. In turn, the PM3 is about 100 times faster than the QC calculations. Thus, with ReaxFF we hope to be able to study complex reactions in hydrocarbons.

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ReaxFF: A reactive force field

$$E_{system} = \underbrace{E_{bond} + E_{vdWaals} + E_{Coulomb}}_{\text{2-body}} + E_{val,angle} + E_{tors}$$

2-body   3-body   4-body

$$+ \underbrace{E_{over} + E_{under}}_{\text{multi-body}}$$

multi-body

Total energy is expressed as the sum of various terms describing individual chemical bonds

All expressions in terms of bond order

All interactions calculated between ALL atoms in system…

No more atom typing: Atom type = chemical element

Example: Calculation of bond energy

$$E_{system} = E_{bond} + E_{vdWaals} + E_{Coulomb} + E_{val,angle} + E_{tors} + E_{over} + E_{under}$$

$$E_{bond} = -D_e \cdot BO_{ij} \cdot \exp\left[p_{be,1} \left(1 - BO_{ij}^{p_{be,1}} \right) \right]$$

Bond energy between atoms *i* and *j* does not depend on bond distance

Instead, it depends on bond order

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Bond order functions

BO goes smoothly from 3-2-1-0

sp³ sp² sp

(1) Bond order
Sigma-bond
Pi-bond
Double pi bond
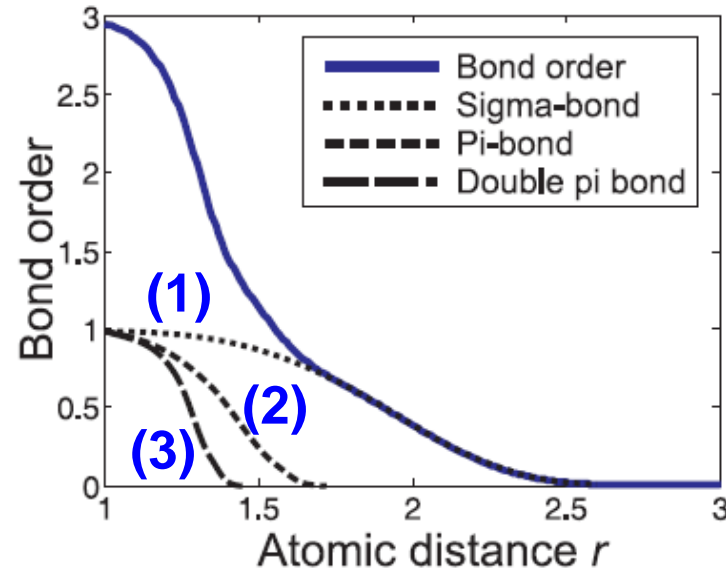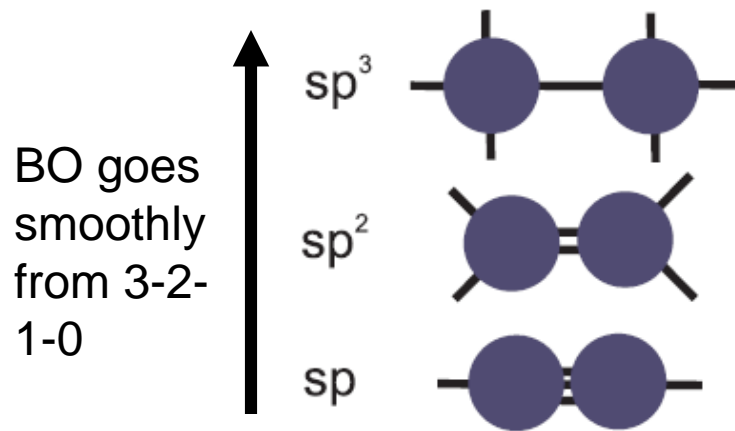
$$\text{BO}_{ij} = \exp\left[\alpha_\sigma \cdot \left(\frac{r_{ij}}{r_0} \right)^{\beta_\sigma} \right] + \exp\left[\alpha_\pi \cdot \left(\frac{r_{ij}^\pi}{r_0} \right)^{\beta_\pi} \right] + \exp\left[\alpha_{\pi\pi} \cdot \left(\frac{r_{ij}^{\pi\pi}}{r_0} \right)^{\beta_{\pi\pi}} \right]$$

(1) **(2)** **(3)**

Characteristic bond distance

All energy terms are expressed as a function of bond orders

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Illustration: Bond energy

$$E_{bond} = -D_e^{\sigma} \cdot BO_{ij}^{\sigma} \cdot f(BO_{ij}^{\sigma}) - D_e^{\pi} \cdot BO_{ij}^{\pi} - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi}$$

10
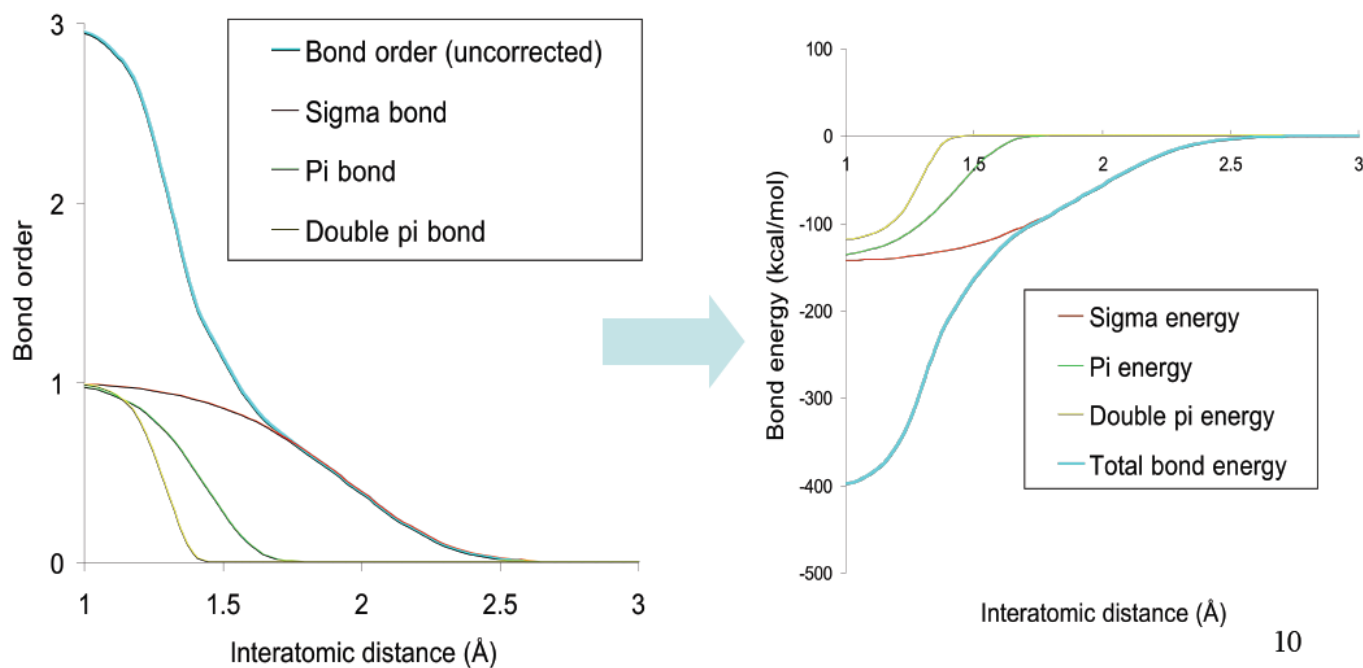
vdW interactions

$$E_{system} = E_{bond} + \boxed{E_{vdWaals}} + E_{Coulomb} + E_{val,angle} + E_{tors} + E_{over} + E_{under}$$

- Accounts for short distance repulsion (Pauli principle orthogonalization) and attraction energies at large distances (dispersion)

- Included for all atoms with shielding at small distances

$$E_{vdWaals} = D_{ij} \cdot \left\{ \exp\left[\alpha_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{vdW}}\right)\right] - 2 \cdot \exp\left[\frac{1}{2} \cdot \alpha_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{vdW}}\right)\right]\right\}$$

$$f_{13}(r_{ij}) = \left[r_{ij}^{\lambda_{29}} + \left(\frac{1}{\lambda_w}\right)^{\lambda_{28}}\right]^{1/\lambda_{28}}$$
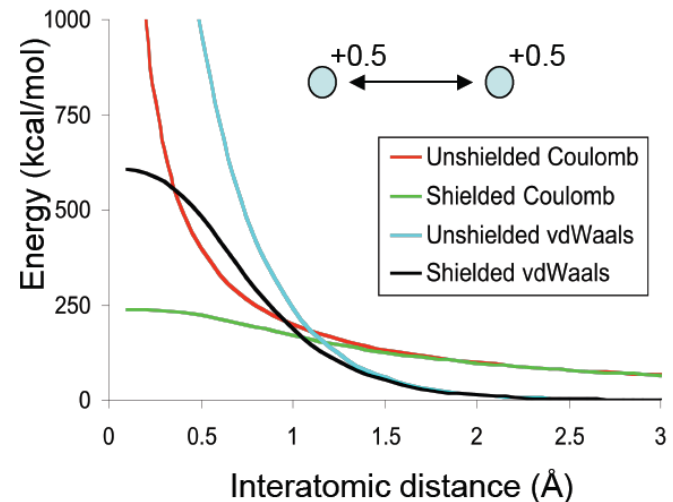
Resulting energy landscape
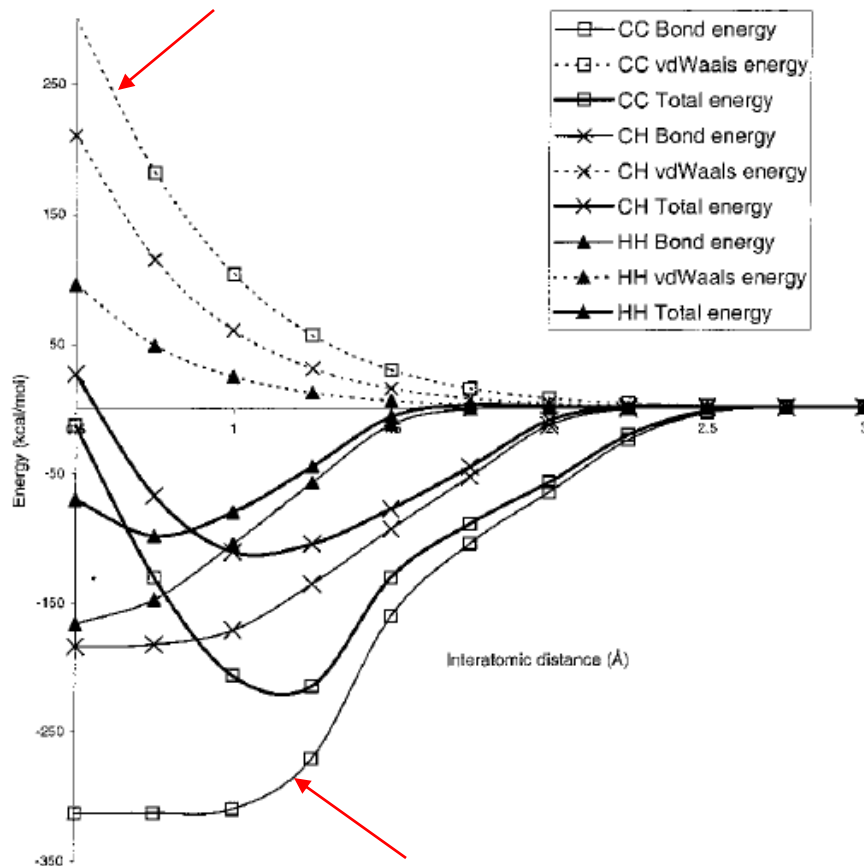
Contribution of E_{bond} and vdW energy

C-C stretching in ethane (bond dissociation)


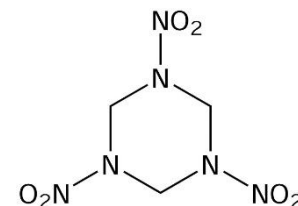Around the equilibrium bond length
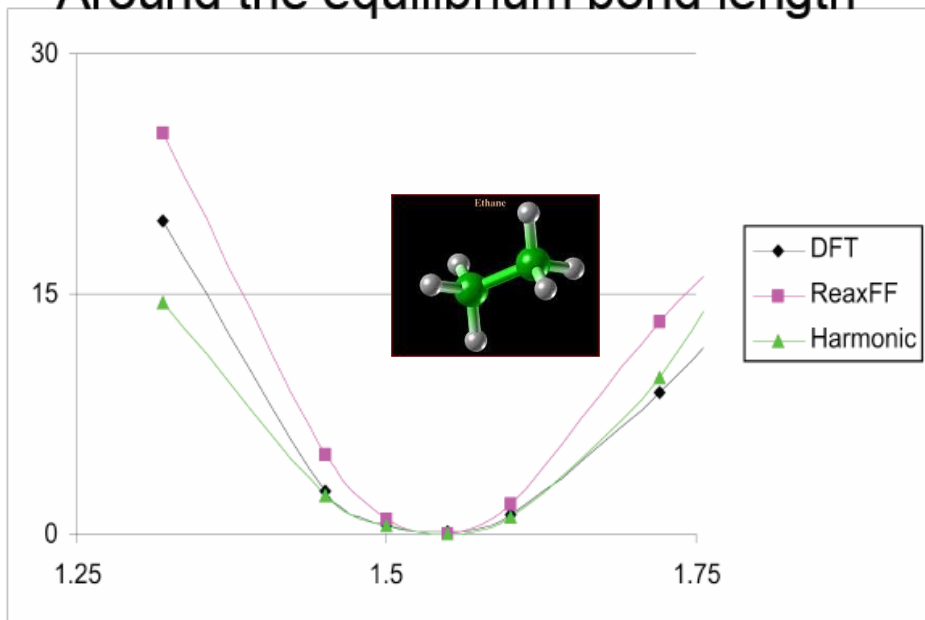
Full dissociation curve
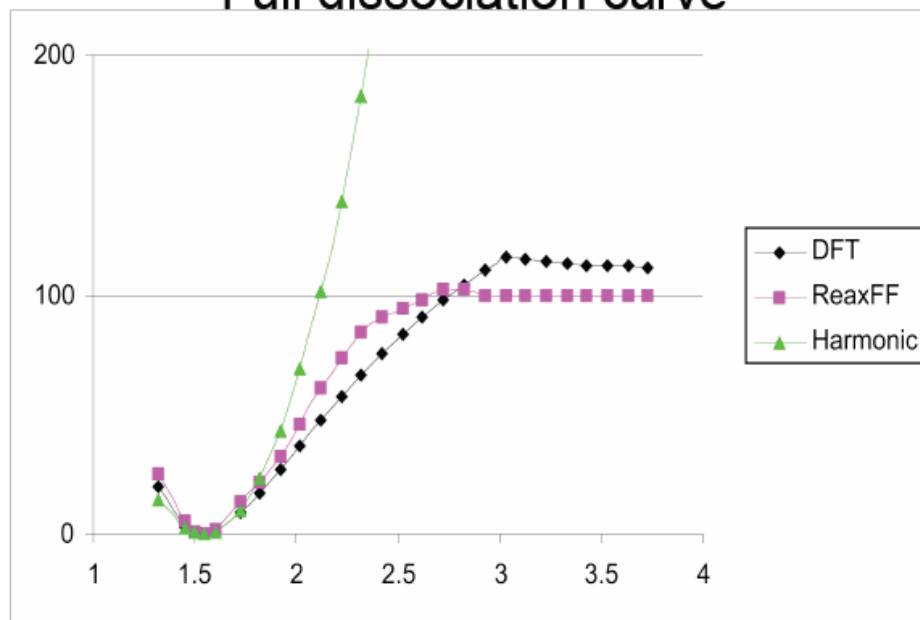
- Although the harmonic approximation can describe the bond stretching around the equilibrium it cannot describe the bond dissociation.
- Harmonic force field needs to use multiple atom types to distinguish single, double and triple bonded carbons.

After: A. V. Duin

Training ReaxFF from quantum mechanics (DFT)
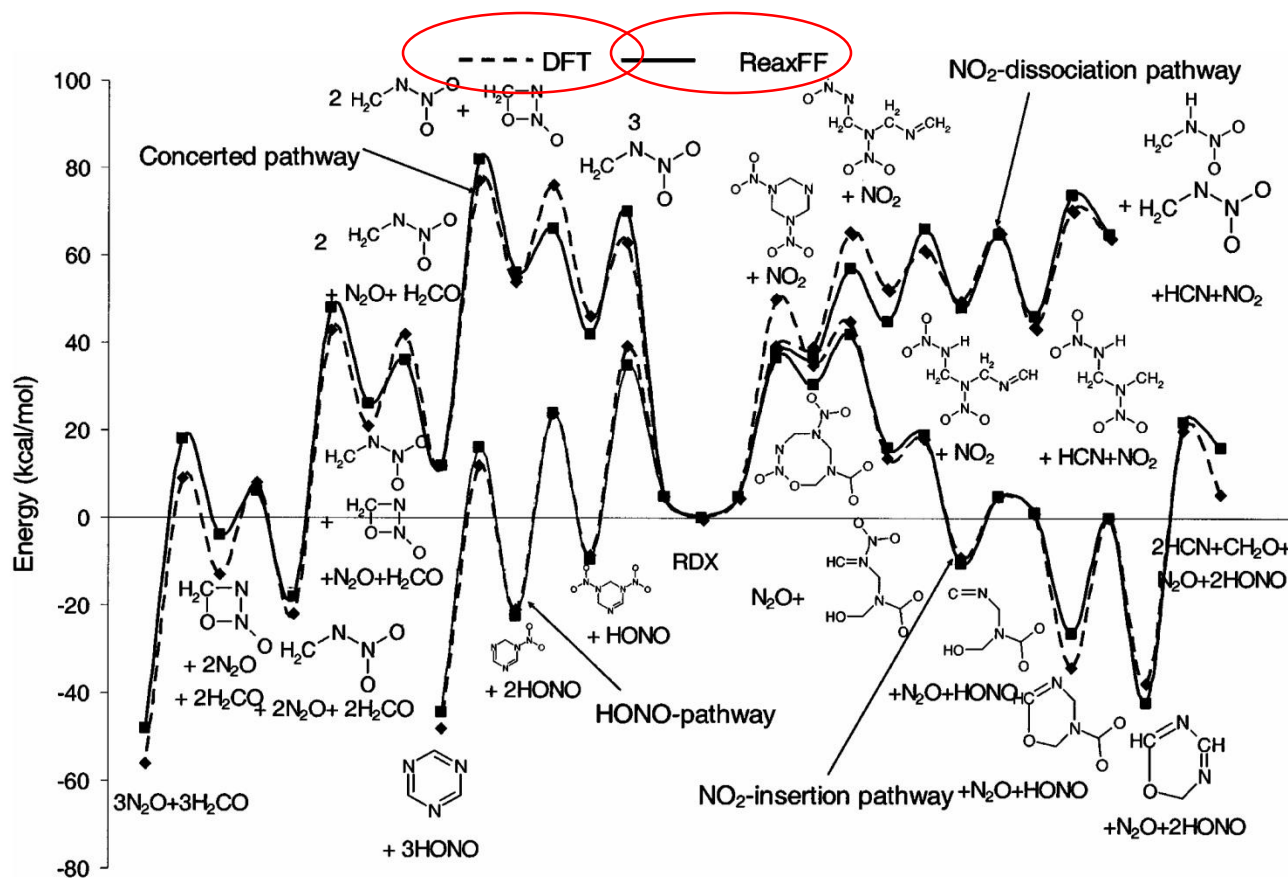
Unimolecular decomposition of RDX

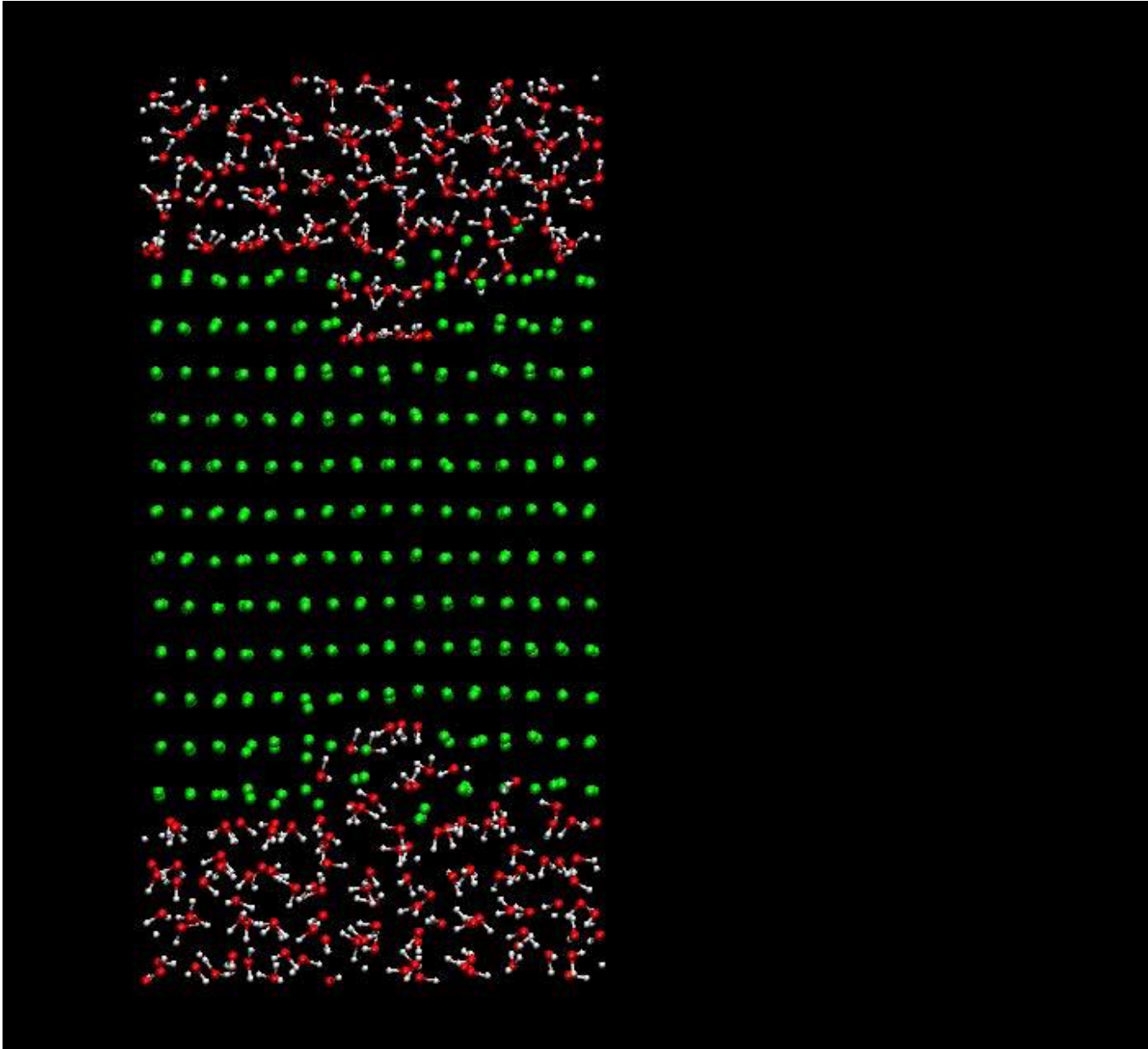A. Strachan *et al.*, *JCP*, 122, 054502, 2005 *(paper posted on Stellar)*

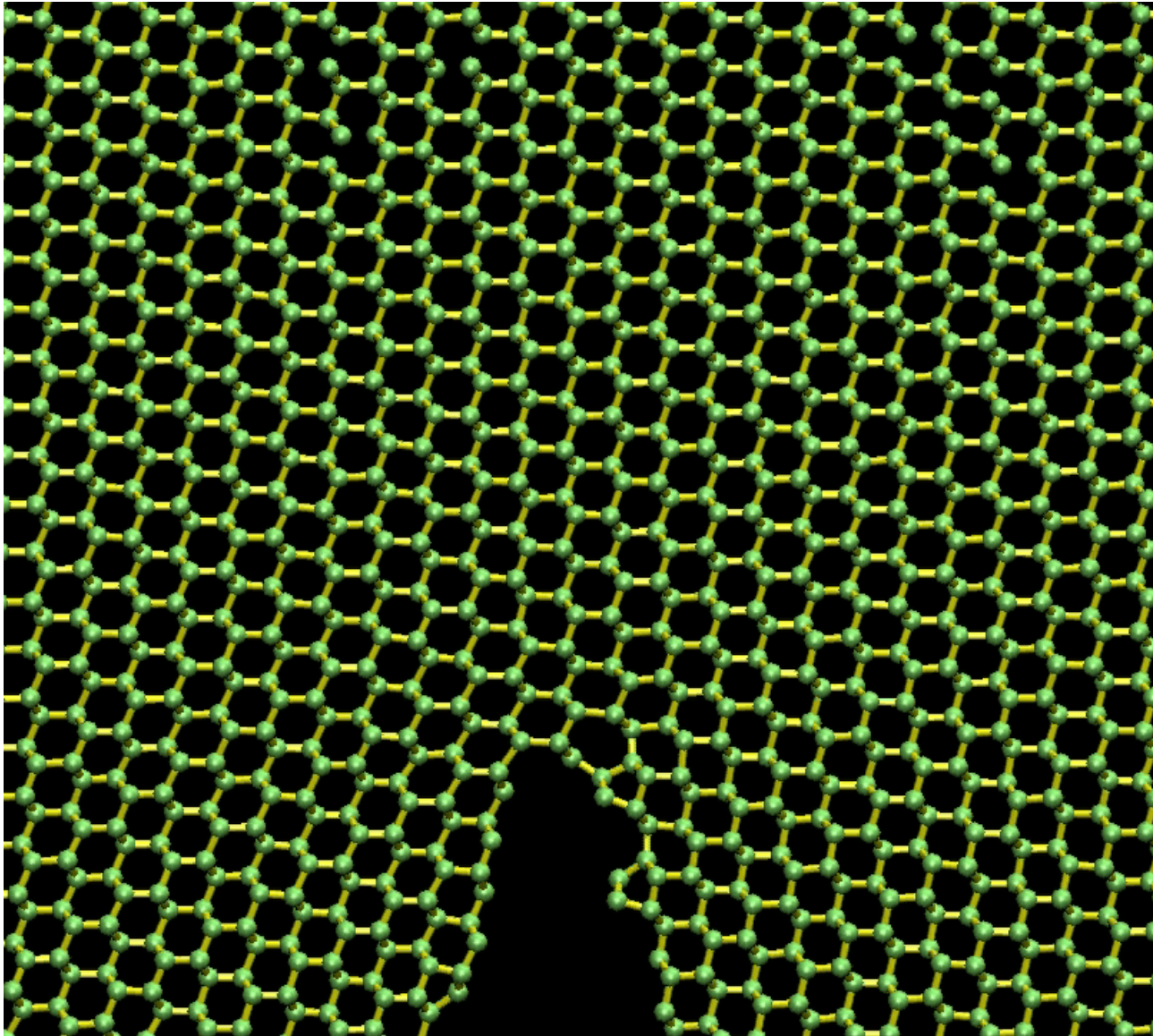# Mg-water interaction: How to make fire with water

Mg

Mg – water interaction – ReaxFF MD simulation

Fracture initiation and instabilities

Computational expense (comparison with QM/DFT)

x 1000,000

- QM (DFT)
- ReaxFF

-ReaxFF allows for reactive MD-simulations on systems containing more than 1000 atoms
- ReaxFF is 10-50 times slower than non-reactive force fields

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A. Duin et al., 2001-2006