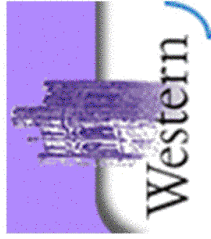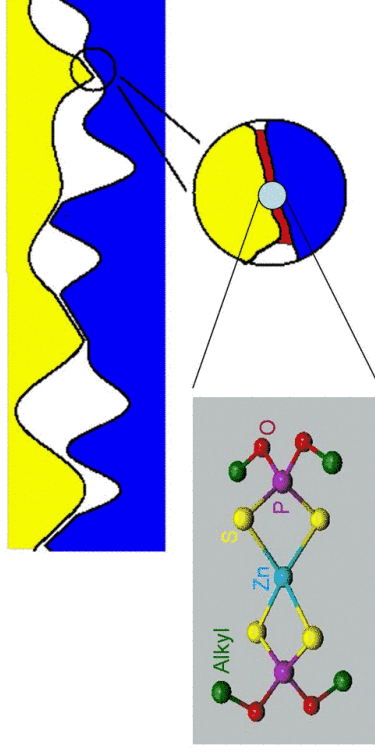# Energy Dissipation Mechanisms at the Nanometer Scale:
Computer Simulations

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*Western*

Acknowledgments

Outline

Small-Scale Mechanisms of _interlocking_ and _dissipation_

- geometric interlocking (why egg cartons don't explain much)

- other interlocking mechanisms

- role of instabilities / molecular hysteresis

- interlocking and instabilities in:
  boundary lubricants (flat surfaces)
  boundary lubricants (curved surfaces)
  unlubricated, rough, elastic contacts

- chemistry-induced interlocking
  nanotubes
  anti-wear films

Energy Dissipation Mechanisms ...

Geometric interlocking

$$F_s = \mu_s L$$
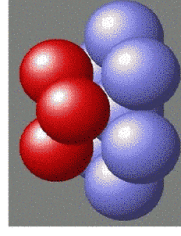
Amontons, Euler, Coulomb:
surfaces are rough ➔
geometric interlocking at
small length scales
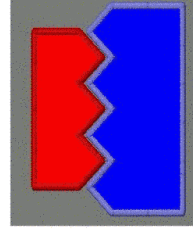
Bélidor (≈1750)
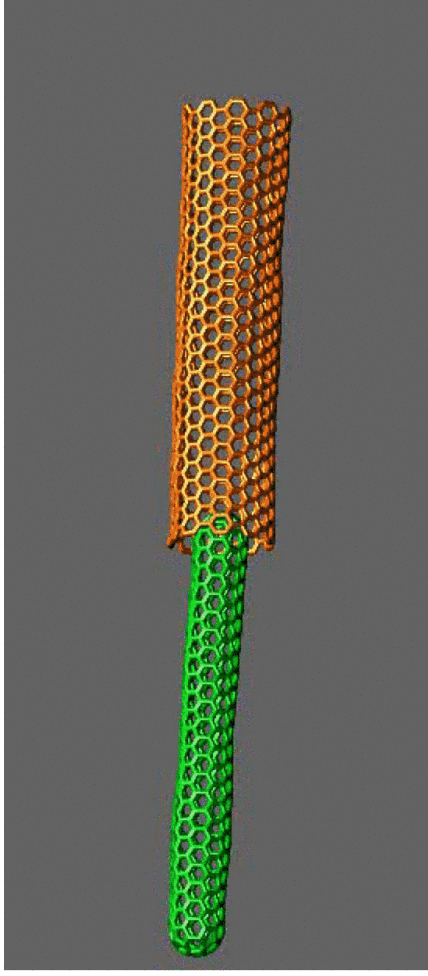spherical caps on surfaces
➔ $\mu_s \approx 0.34$

But: Surfaces usually don't match
and what about kinetic friction?

Energy Dissipation Mechanisms ...

Geometric interlocking

Nanotube embedded in another *commensurate* nanotubes

$\Rightarrow$ large F_s $\Rightarrow$ large, instantaneous, lateral forces

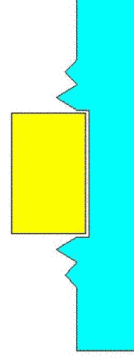Tangney, Louie, Cohen, PRL 93, 065503 (2004)

Thanks to Paul Tangney

Energy Dissipation Mechanisms ...

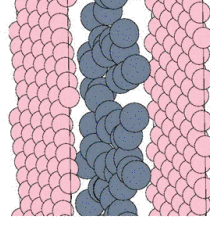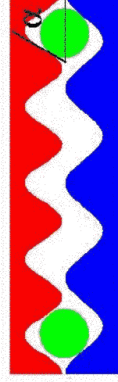## Other interlocking mechanisms

- **elastic** deformation allows
  for interlocking (Coulomb)
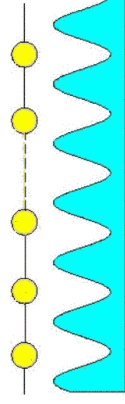
- **plastic** deformation
  (Bowden and Tabor)

- **boundary lubricants**

- cold welding, **tribo-chemical reactions**

Energy Dissipation Mechanisms ...

Role of instabilities

- interlocking does not explain **kinetic friction** or **dissipation**

Prandtl model
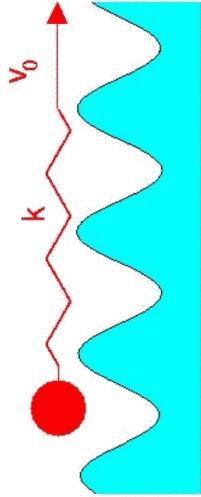
if V'' exceeds k
$\Rightarrow F_k$ is finite and relatively independent of v_0
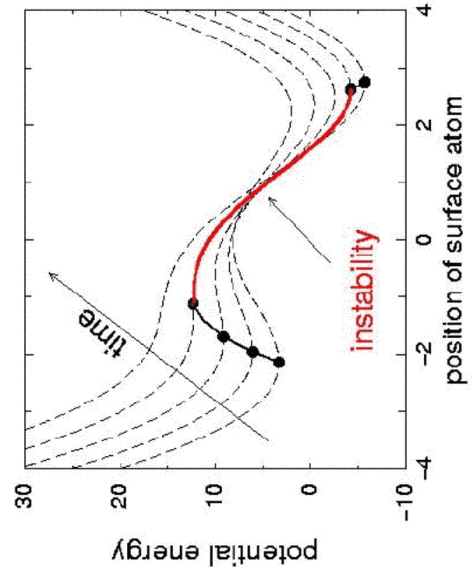
Energy Dissipation Mechanisms …

Instabilities in boundary lubricants
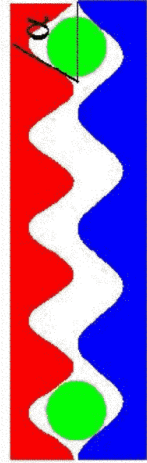
qualitative argument:
surface has to climb
up a slope α ➜ **μ = tan α**

G. He, MHM, M.O. Robbins,
Science 284, 1650 (1999)

accounts for static friction

Do boundary lubricant **automatically** lead to F_k?   **No.**

Do boundary lubricants **typically** lead to F_k?   **Yes.**

Energy Dissipation Mechanisms …

Instabilities in boundary lubricants

Do boundary lubricants **automatically** lead to F_k?   **No.**
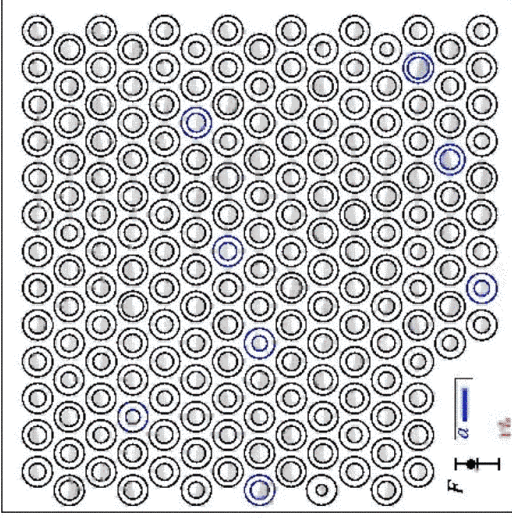
Two **commensurate** walls separated by a **single-layer** lubricant:

Theory: MHM, PRL **89**, 224301 (2002)
Snapshots: MHM, MWWT **35**, 603 (04)
Movies: publish.uwo.ca/~mmuser
show movie in external player

Energy Dissipation Mechanisms …

Instabilities in boundary lubricants

Do boundary lubricants **typically** lead to F_k?   **Yes.**

Two **incommensurate** walls separated by a **single-layer** lubricant:

Theory: MHM, PRL **89**, 224301 (2002)
Snapshots: MHM, MWWT **35**, 603 (04)
Movies: publish.uwo.ca/~mmuser
show movie in external player

Energy Dissipation Mechanisms …

Instabilities in boundary lubricants

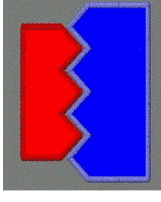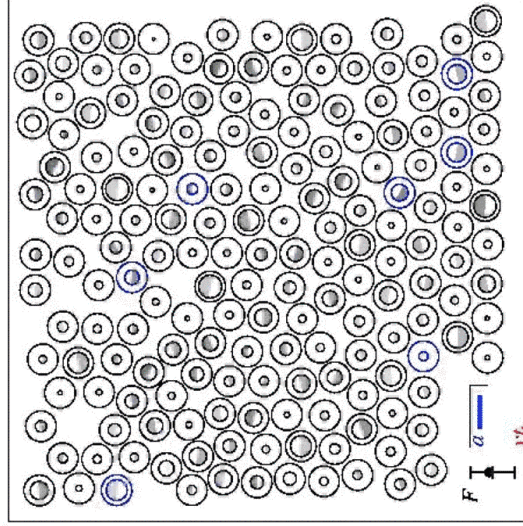Do boundary lubricants **typically** lead to **typical** F_k? **Yes.**

G. He and M. O. Robbins, Tribol. Lett. **10**, 7 (2001).

$$F_k(v) \sim F_k(v_0) + \Delta \ln(v/v_0)$$

MHM, PRL **89**, 224301 (2002)
M. Aichele and MHM, PRE **68**, 016125 (2003)

Energy Dissipation Mechanisms ...
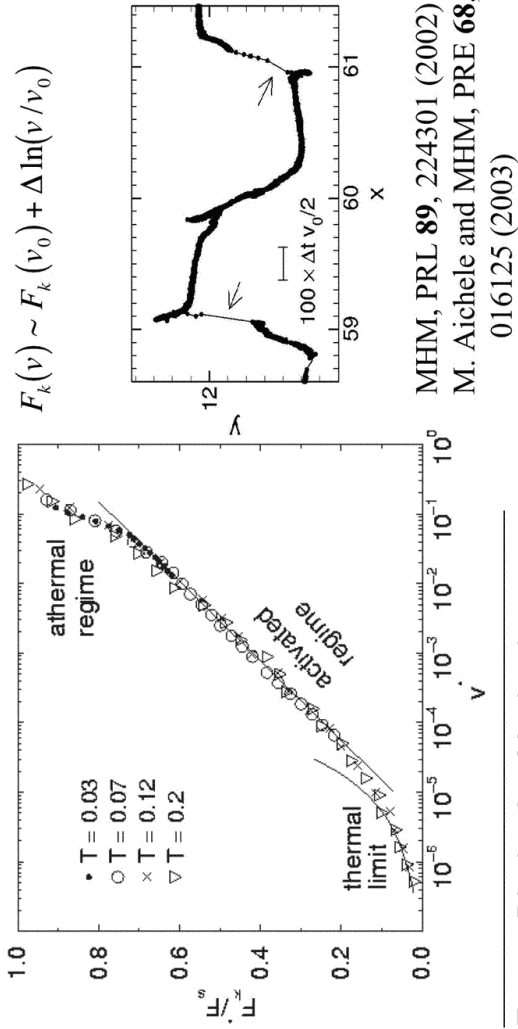
Boundary lubricants

- **flat interfaces**: $F \sim L$
- **curved** interfaces: may be different in detail (squeeze out)

top view

load map
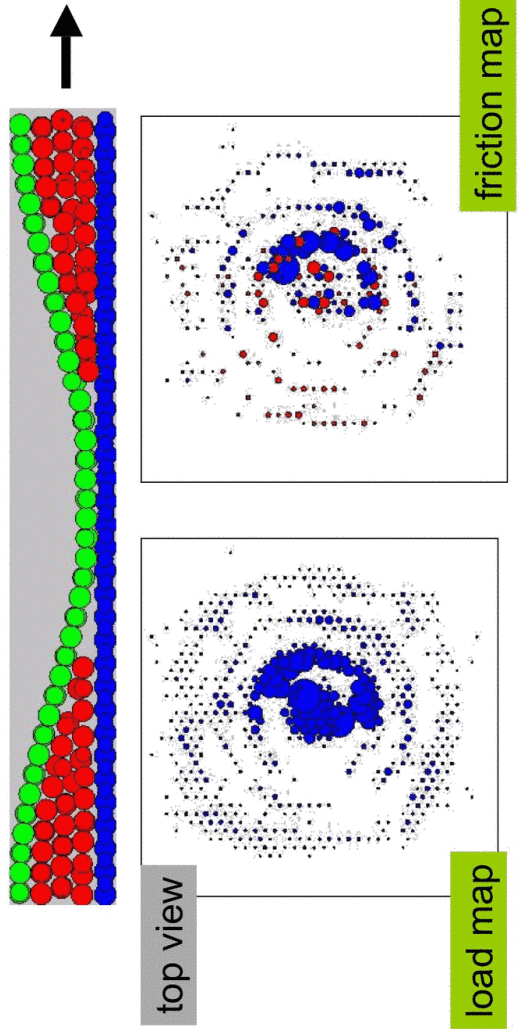
friction map

L. Wenning and MHM,
Europhys. Lett. **54**, 693 (2001)

Energy Dissipation Mechanisms ...

Elastic instabilities

Can the competition of elasticity and roughness (on long length scales) lead to friction without *local* friction mechanisms?

if $V'' > k \Rightarrow F_k$ is finite

on local scale: atypical

$k_{physical} = 2\,GPa * 3\,A$

$k_{covalent} = 20\,GPa * 2\,A$

covalent
physical
covalent

v_0
k
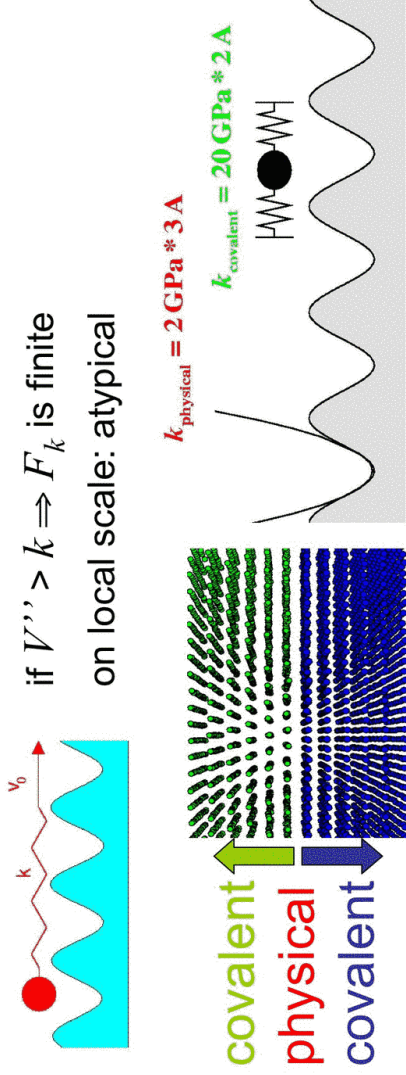
Do larger length scales change the picture?

Energy Dissipation Mechanisms …

Elastic instabilities
- fractal on fractal -

Do larger length scales change the picture?

$L = 0.01$

$L = 0.1$

- potential such that "Amontons's law" holds locally: $F_{lat} = (\nabla h)L$

$$C(\Delta r) = \left\langle \{h(\vec{r}) - h(\vec{r} + \Delta\vec{r})\}^2 \right\rangle \propto \Delta r^{2H} \quad H \text{ Hurst roughness exponent}$$

$$\tilde{S}(\vec{q}) = \left\langle \tilde{h}(\vec{q})\tilde{h}^*(\vec{q}) \right\rangle \propto q^{-2H-d}\delta(\vec{q}-\vec{q}') \quad \text{for} \quad \frac{2\pi}{\lambda_{long}} \leq q \leq \frac{2\pi}{\lambda_{short}}$$

- elastic slider: mass points $m = 1$, springs $k = 1$, length $a = 1$
  1D: elastic chain (maps onto Frenkel-Kontorova model)
  2D: trigonal lattice (Poisson ratio: ν=0; ν=1/3)
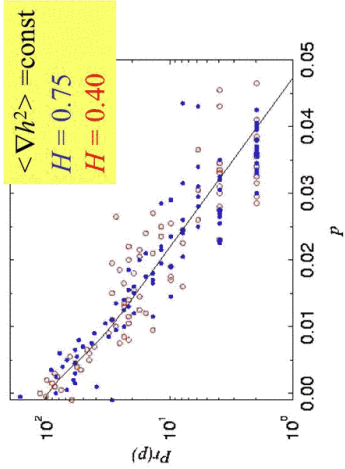 3D: s.c. lattice with 2nd neighbor coupling

C. Campana and MHM, to be submitted

Energy Dissipation Mechanisms …

Elastic instabilities

- fractal on fractal -

- reproduces almost exactly results for the 1D FK model
- models of elastic, non-adhesive contacts suggest:

$Pr(p)=f(\langle\nabla h^2\rangle)\sim\exp(-p/p')$ for $p\to\infty$ Hyun et al., PRE **70**, 026117 (2004)

1+1 dimensional surface

Friction :

$$H = 0.75; \sqrt{\langle(\nabla h)^2\rangle} = 0.35$$

$$L = 0.1B$$

$$\lambda_c^{short} = 4a ; \lambda_c^{long} = 1024\,a$$

$$\Rightarrow \mu_s = 2\times10^{-4}$$

C. Campana and MHM, to be submitted

Measurable friction coefficients:
Presence of (local) buckles

Energy Dissipation Mechanisms …

$\langle\nabla h^2\rangle$ =const
H = 0.75
H = 0.40

Elastic instabilities

- Ni(100) on Ni(100) -

- local roughness seems key factor for friction coefficients
see also Mark's recent Nature paper

Simulations: **Yue Qi** et al., Phys. Rev. B 66, 085420 (2002)

inc./smooth   comm./smooth

inc./rough   comm./rough

experiment
rough
flat

Rough

flat

Static Friction Coefficients

Lattice Misorientation (degrees)

Energy Dissipation Mechanisms …

Left panel

Chemistry-induced interlocking
- *carbon nanotubes -*

• friction between nanotubes (chemically realistic potentials)
Stuart, Piotrowski, and MHM, J. Phys. Chem. B (to be submitted)

$F < 0.1$ nN / vacancy

inner: infinite (PBC)
outer: **H-terminated**
⇑   superlubric

outer: **unterminated**
⇑   superlubric

outer: **point defects**
⇑   superlubric

Energy Dissipation Mechanisms …
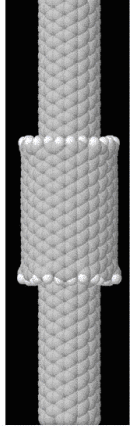
Right panel

Chemistry-induced interlocking
- *carbon nanotubes -*

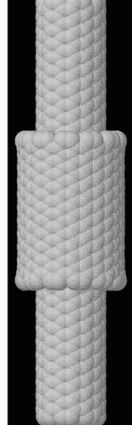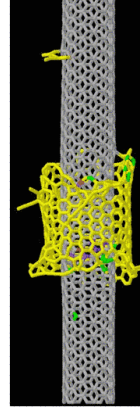• friction between nanotubes (chemically realistic potentials)
Stuart, Piotrowski, and MHM, J. Phys. Chem. B (to be submitted)

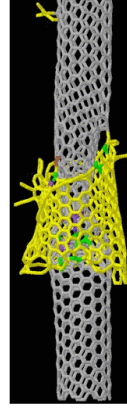simulations: $F < 0.1$ nN ; $\sigma < 0.02$ MPa
experiments: $F = 100$ nN

• simulations do not include fracture process of outer tube

snapshot following fracture

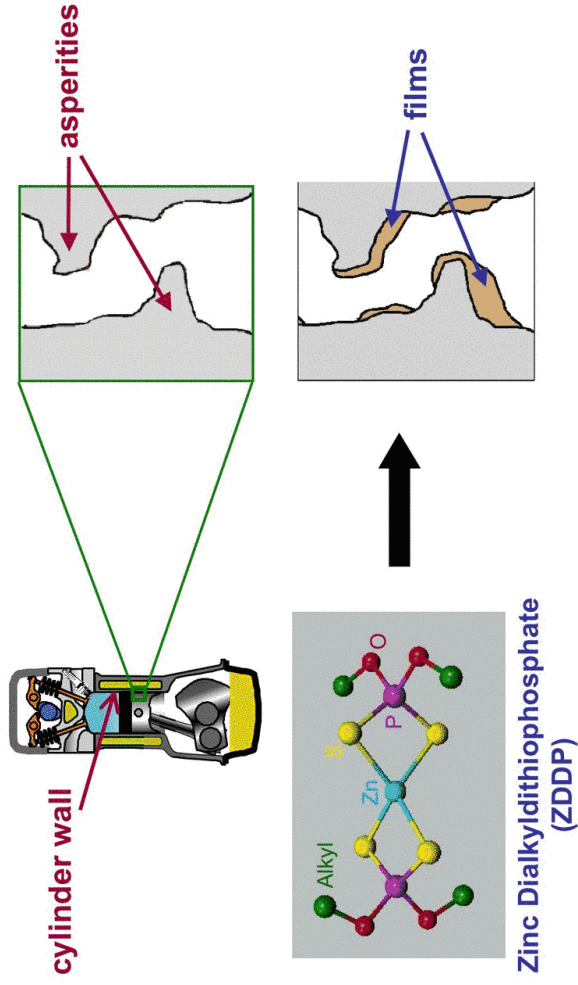snapshot following sliding
simulations: $F = 50$ nN

Energy Dissipation Mechanisms …

Chemistry-induced interlocking
- formation and functionality of anti-wear additives -

asperities

films

cylinder wall

Zinc Dialkyldithiophosphate (ZDDP)

Alkyl

O

P

S

Zn

Energy Dissipation Mechanisms …

Anti-wear films



Alkyl

O

P

S

Zn

ZDDP

- invented in the 1930's
- optimized for steel and cast iron surfaces

new additives sought-after:

- ZDDPs ineffective on lightweight materials, such as aluminum
- Zn, S and P atoms damage catalytic converters

phenomenology of ZDDP anti-wear pads well known

- theories for anti-wear pad (AWP) formation unconvincing
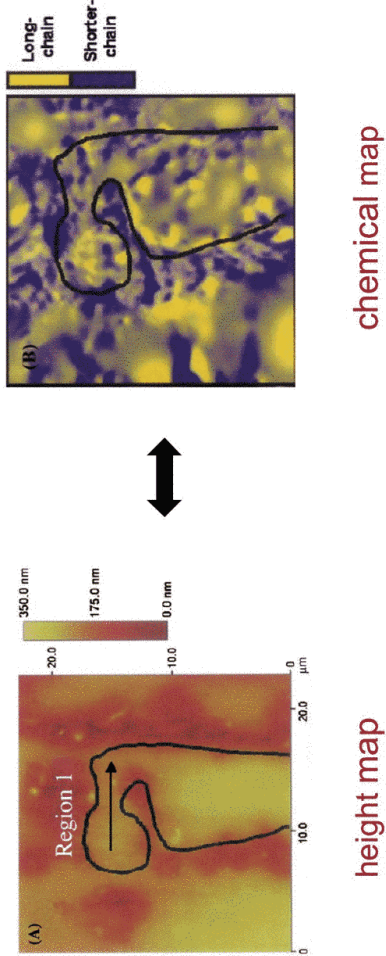- no molecular theory of AWP functionality

⇒ rational design of new AW additives not possible

Energy Dissipation Mechanisms …

Anti-wear films
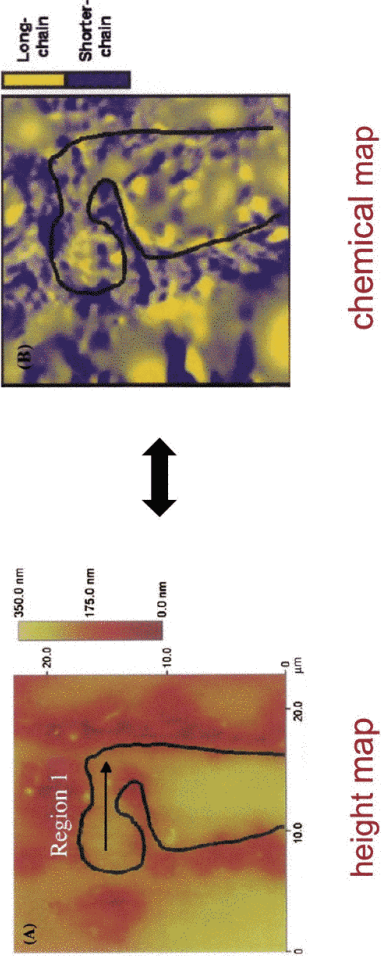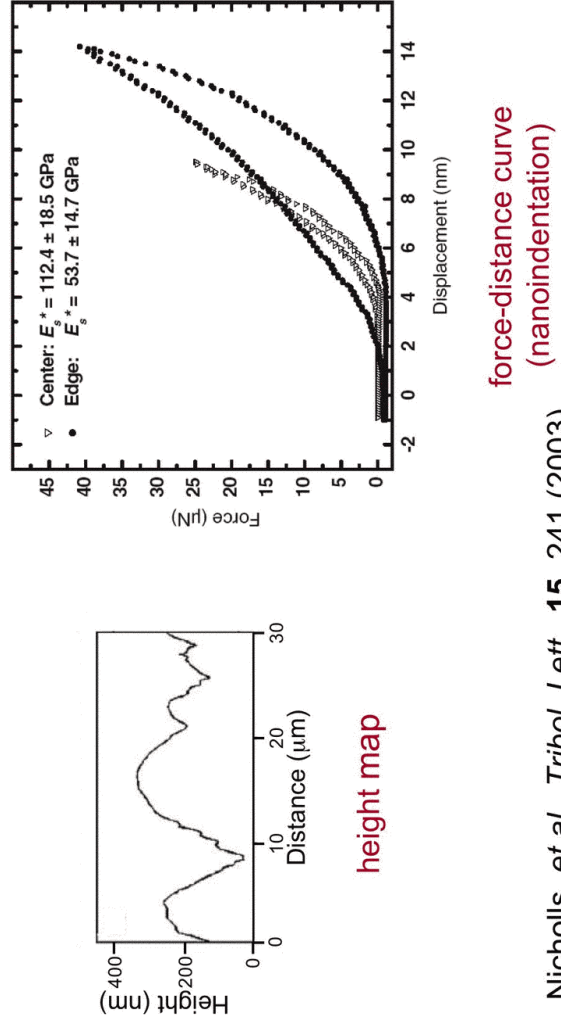*- ZDDP film phenomenology -*

height map

chemical map
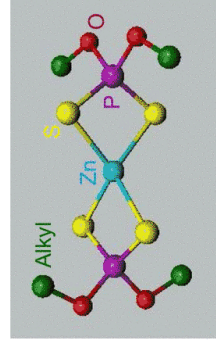
spectra on tops of pads reminiscent of "longer" zinc phosphate chains

Nicholls *et al., Tribol. Lett.* **17**, 205 (2004)

Energy Dissipation Mechanisms …

Anti-wear films
- ZDDP film phenomenology -

force-distance curve
(nanoindentation)

height map

Nicholls, *et al.*, *Tribol. Lett.*, **15**, 241 (2003)

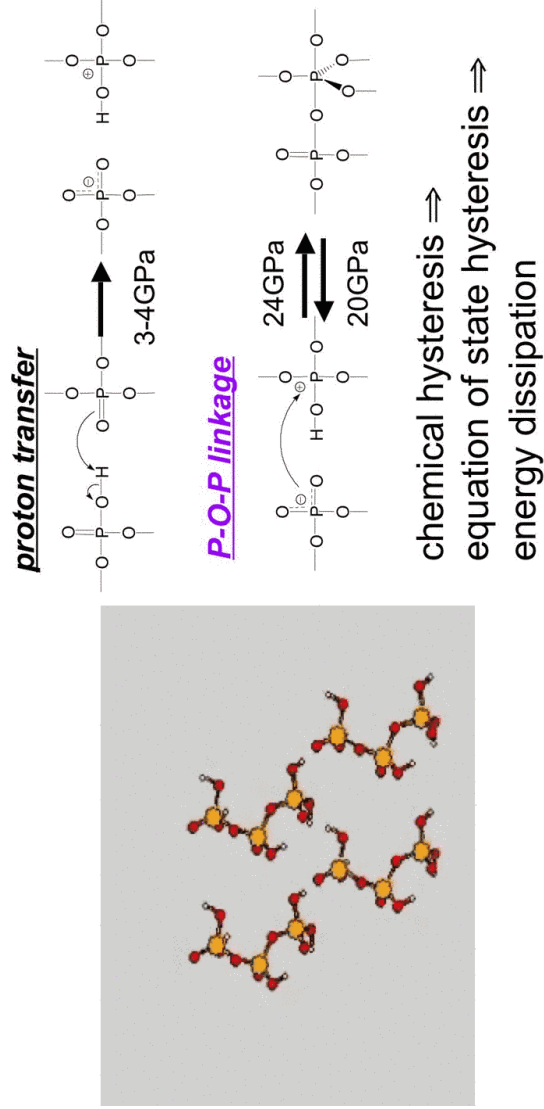Energy Dissipation Mechanisms …

Anti-wear films
- ZPs in microcontacts -

Pads form and function on asperities

Theory must consider extreme conditions in contacts

pressure   → theoretical yield strength

temperature → melting temperature

Study response of decomposition products to ρ and T
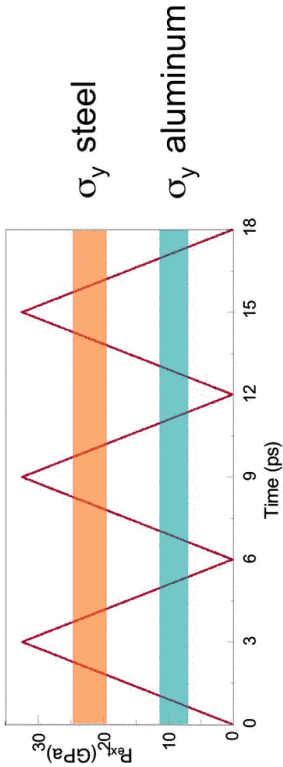
σ_y steel

σ_y aluminum

Energy Dissipation Mechanisms …

Anti-wear films
- ZPs in microcontacts -

proton transfer

3-4GPa

P-O-P linkage

24GPa

20GPa

chemical hysteresis ⇒
equation of state hysteresis ⇒
energy dissipation

Mosey, Woo, MHM, PRB **72**, 054124 (2005)

Energy Dissipation Mechanisms ...

Anti-wear films
- structural changes in phosphates -

no cross-linking   moderately cross-linked   no cross-linking

P↑   P↓
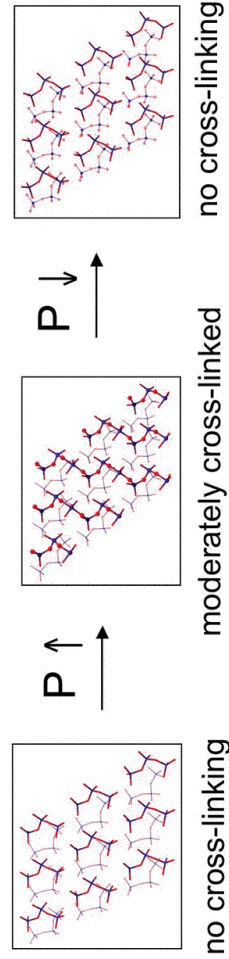
Pure Phosphates:
cannot serve as AWPs, because do not form pads
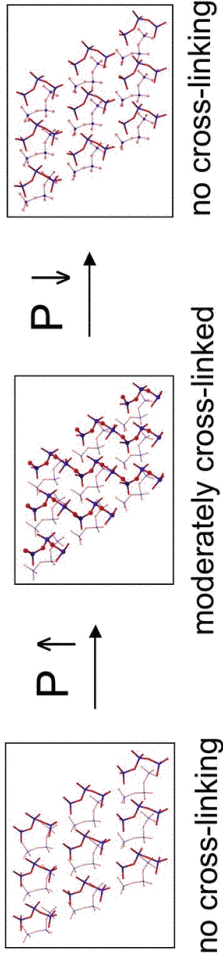
Energy Dissipation Mechanisms ...

Anti-wear films
- structural changes in phosphates -

Pure Phosphates:

no cross-linking   P →   moderately cross-linked   P →   no cross-linking

Zinc Phosphates:

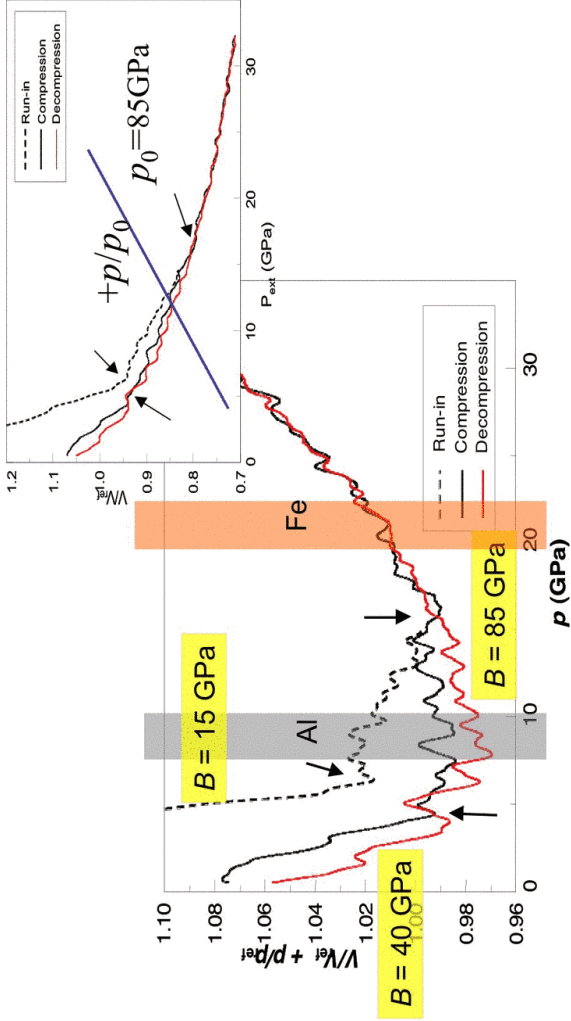no cross-linking   P →   highly cross-linked   P →   moderately cross-linked
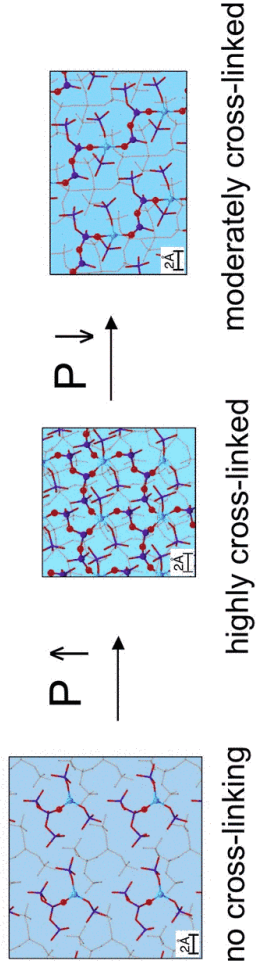
Energy Dissipation Mechanisms ...   Mosey, MHM, Woo, Science **307**, 1612 (2005)

Anti-wear films
- equation of state of ZPs -

$p_0 = 85\,GPa$

$+p/p_0$

Fe

B = 15 GPa

Al

B = 85 GPa

B = 40 GPa

Energy Dissipation Mechanisms ...   Mosey, MHM, Woo, Science **307**, 1612 (2005)

Anti-wear films
- comparison to experiment -

- chemically-connected, hard pads form where *p* is high

  Nicholls, *et al.*, *Tribol. Lett.*, **2004**, *17*, 205
  Nicholls, *et al.*, *Tribol. Lett.*, **2003**, *15*, 241

- explanation of why ZDDPs do not work on Al

- effects of Ca-containing detergents can be rationalized

  reduces wear on Al   (Norton group)
  increases wear on steel (Varlot, *et al.*, *Wear*, **2001**, *249*, 1029)

  . . . and many other observation (growth rate, tempering, …)

Energy Dissipation Mechanisms …

Conclusions

- kinetic friction requires the presence of instabilities
  - interlocking alone may not be enough

- instabilities can often be categorized
  - elastic instabilities
  - plastic instabilities
  - erratic motion in boundary lubricants
  - pressure or sliding-induced chemical reactions

- the last layer plays a tremendously important role

Energy Dissipation Mechanisms …