Molecular Tribology

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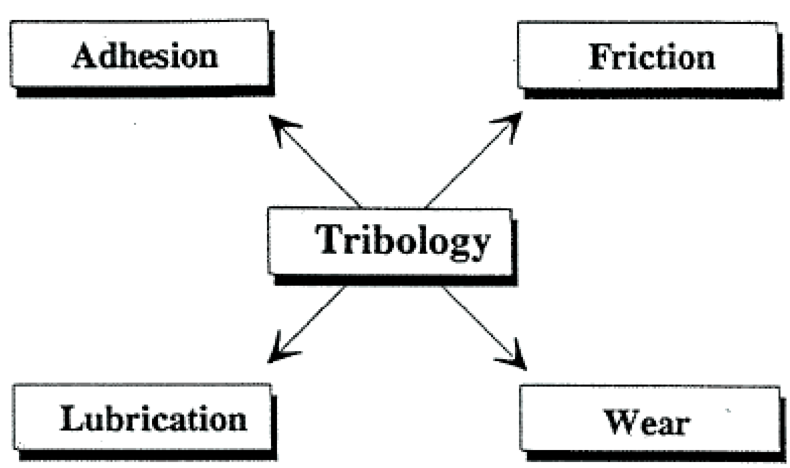
Tribology

The science of *Tribology* (Greek *tribos*: *rubbing*) concentrates on *Contact Mechanics of Moving Interfaces* that generally involve energy dissipation



Thematic Basis

- *Tribology* (friction, lubrication, adhesion and wear), plays an important role in mankind's efforts to conserve energy.
- Friction and drag alone account for about 1/3 of the energy needed to run our machines in the industrialized World. This does not account for energy losses due to consequential wear and failure of equipment.
- It is argued that about 1-2 percent of the GDP could be recovered with appropriate tribological solutions that entail
  - besides liquid phase lubrication
  - also effective solid phase solutions.
- The on-going challenge is to connect rational molecular designs to the phenomenological process parameters that (attempt to) describe the energy dissipation during frictional sliding.

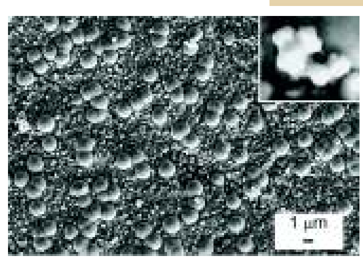
Low Friction Interfaces

- via "liquid" lubrication

  GREASE LUBRICATION (semisolid, high viscosity lubricants)
  - Powdered solid greases with *additives, such as*: Teflon, graphite, molybdenum disulfide
  - Silicone greases
  - Fluoroether-based greases

  OIL LUBRICATION
  - Natural oils (natural product based or synthesized)
  - Mineral oils (crude oil based, or synthetic oils)

- via "solid" coatings and surface modification

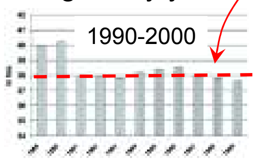


E.g., Nanocomposite coatings for solid self-lubrication (Michael Berger, (2007) Nanowerk LLC)

Lubricants: Scale

Production

- globally/year: 38 megatons (10^9 kg) of lubricants and related functional fluids



1.5 – 2 megatons of lubricant additives

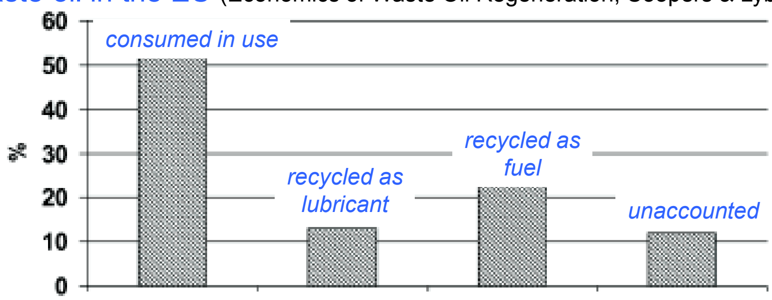
0.7 synthetic lubricant basefluids

(compared to: 400 megatons of total production of chemicals – without mineral oils)

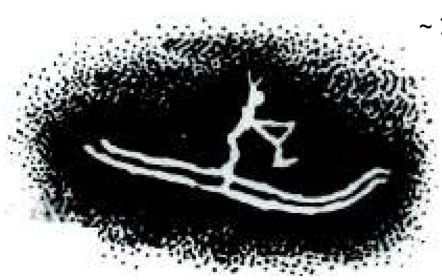
Sources: *Lubricating Oil Additives*, SRI Int., Chem. Econ. Handbook, (1999).
Strategy for a future chemicals policy, Commission of the EU, Brussels (27/2/2001)

➔ The lubricants industry produces ~10 % of the total global chemical production by weight.

Fate of waste oil in the EU (Economics of Waste Oil Regeneration, Coopers & Lybrand, 1998)

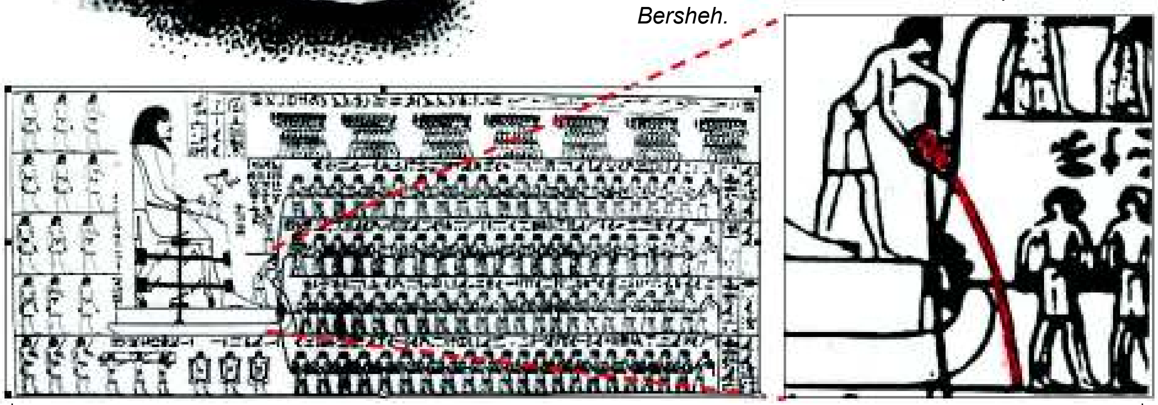


Prehistoric to Ancient Times



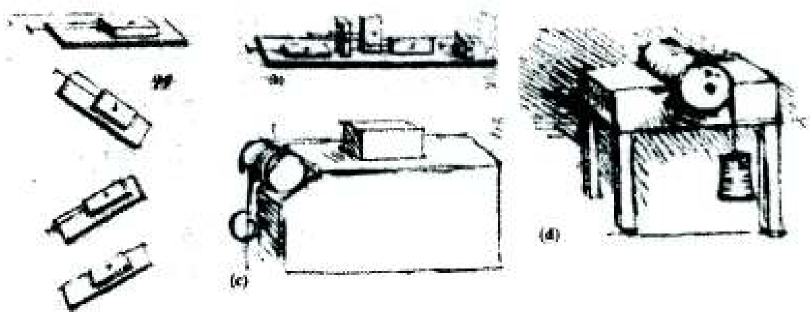
~ 7000 B.C. Northern Norway – Skier in rock carving

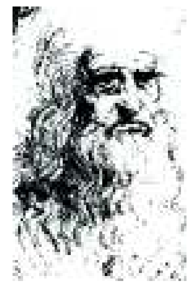
1880 B.C. Egypt – Transport of Eqyptian colossus on the tomb of Tehuti-Hetep. El-Bersheh.



The Historical Laws of Friction

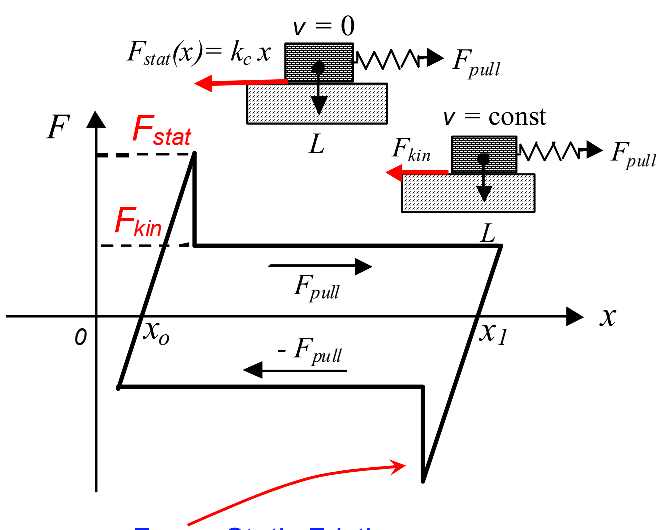
1. The force of friction, F_F, is directly proportional to the applied load L, i.e., $F_F = \mu L$ with the friction coefficient μ. (Amontons' first law)
2. The force of friction is independent of the apparent area of contact A, i.e., $F_F \neq f(A)$. (Amontons' second law)
3. Kinetic friction is independent of the sliding velocity v, i.e., $F_F \neq f(v)$. (Coulomb's law)





Leonardo da Vinci

Dry and Wearless Friction



F_{kin} … Kinetic Friction

What plays a role here?

F_{stat} … Static Friction

Adhesion plays an important role.

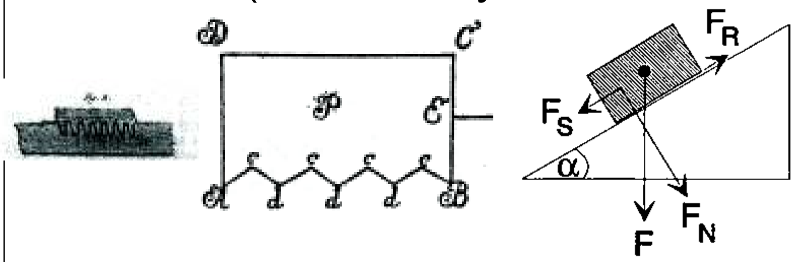
Def.: Friction Coefficient

$$\mu = \frac{F_{kin}}{L}$$

L … Load (normal force)

Friction – Theoretical Models

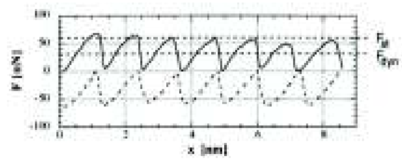
- Euler's (18th century) Asperity Interlocking Model

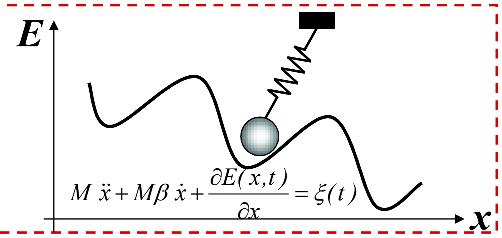


Friction Coefficient:

$$\mu = \tan\alpha - \frac{2s}{gt^2\cos\alpha}$$

Observed for Molecularly Smooth Surfaces



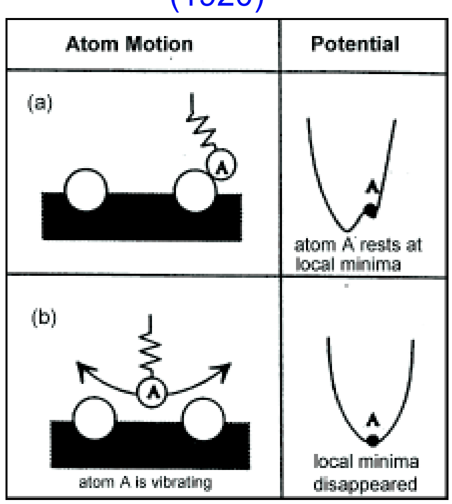


$$M\,\ddot{x} + M\beta\,\dot{x} + \frac{\partial E(x,t)}{\partial x} = \xi(t)$$

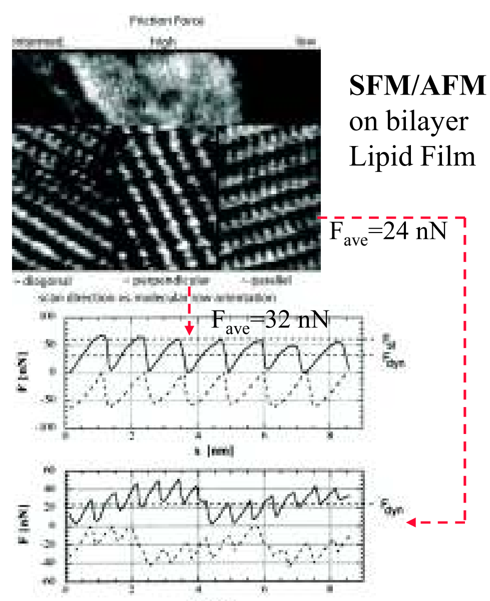
"Dry" Friction: Molecular Stick-Slip

Experimental Verification

Prandtl - Tomlinson Model (1920)

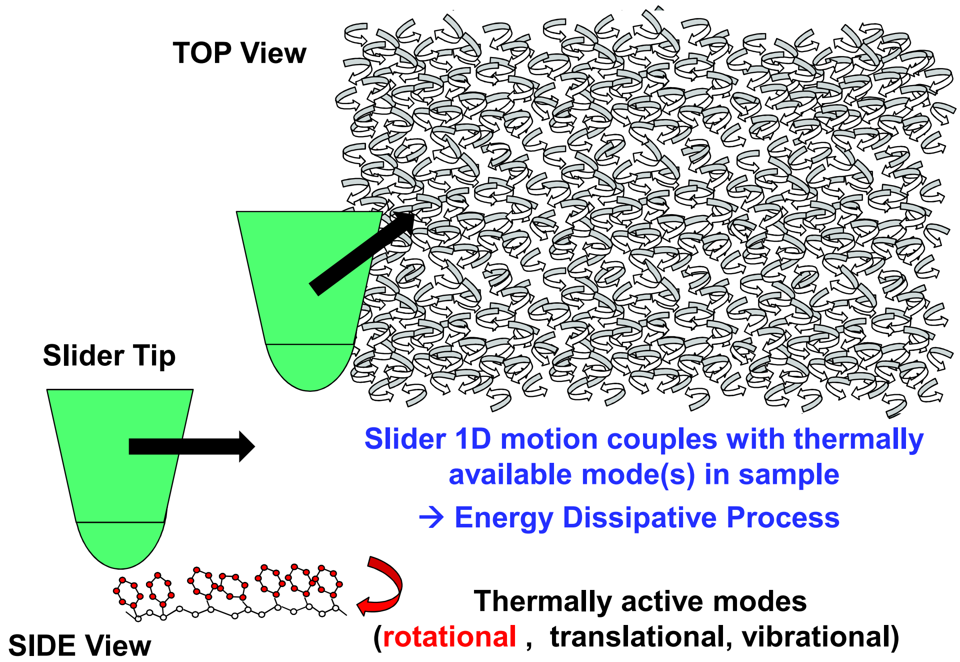


$$M\ddot{x} + M\beta\dot{x} + \frac{\partial E(x,t)}{\partial x} = \xi(t)$$



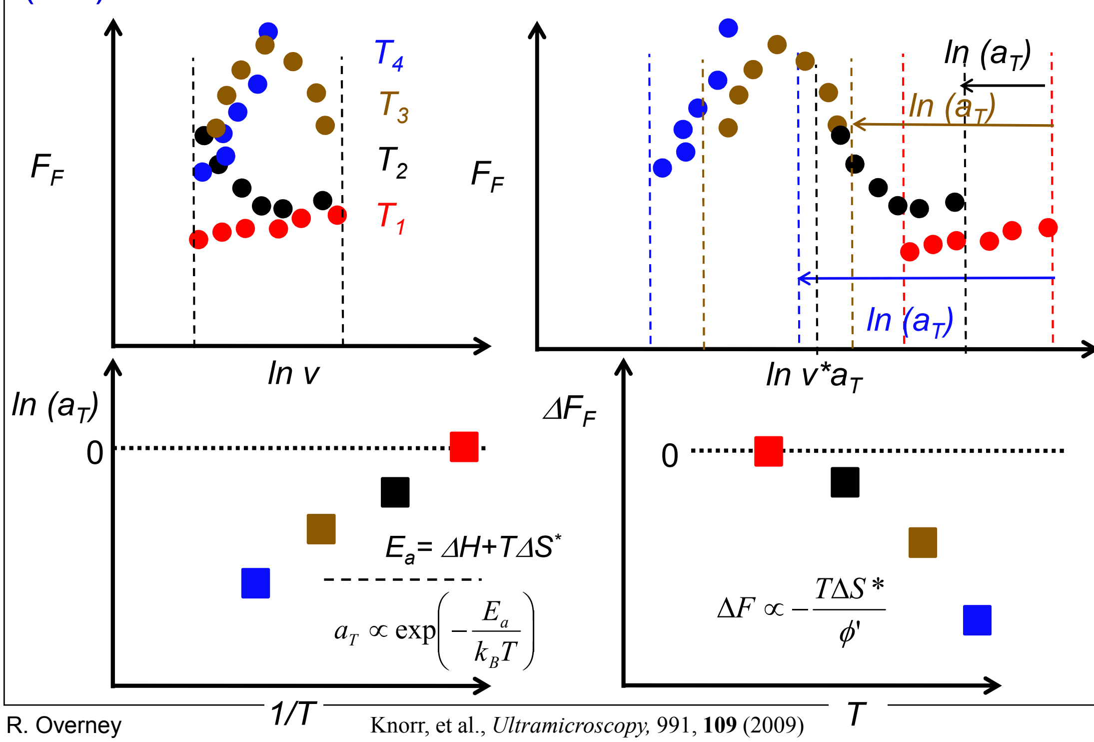
Overney et al., PRL, 72, 3546 (1994)

Coupling with Thermally Active Modes



Time-Temperature Superposition - Intrinsic Friction Analysis (IFA)

Shift Data to form Master Curve: $T_1 = T_R$



Knorr, et al., *Ultramicroscopy,* 991, **109** (2009)

Cooperation Energy and Length

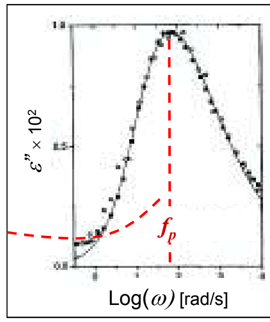
Starkweather:

$$\Delta G^* = RT\left[1 + ln\left(\frac{k_B}{2\pi h}\right) + ln\left(\frac{T}{f_p}\right)\right] + T\Delta S^*$$

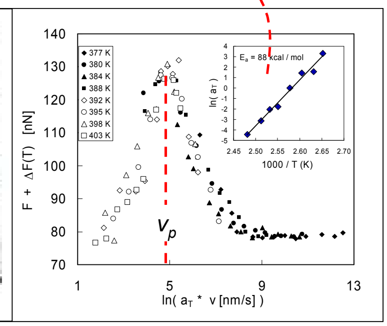
→ $T\Delta S^*$

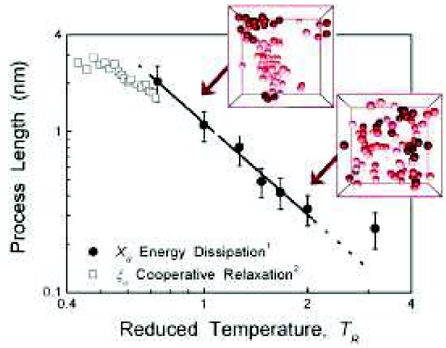
→ $\Delta G^* = \Delta H^* - T\Delta S^*$

Dielectric Loss Spectrum



Intrinsic Friction Analysis





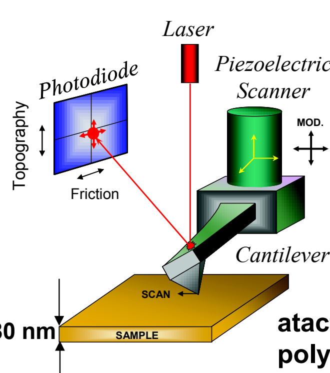
Cooperation Length:

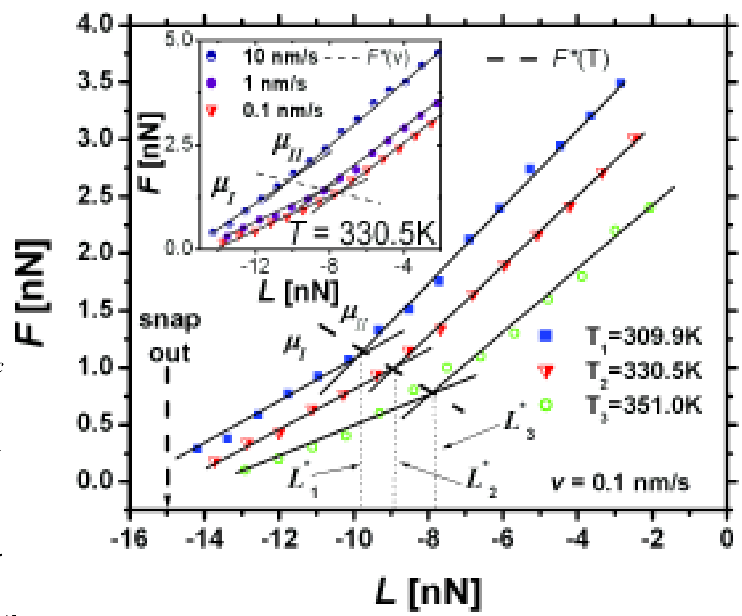
$$\xi \equiv \frac{v_p}{f_p}$$

Frictional Dissipation: Load Distinctive Modes

Material:
Atactic polystyrene (PS)
(M_w=95.5k, Mw/Mn=1.05)

Lateral Force
Microscopy





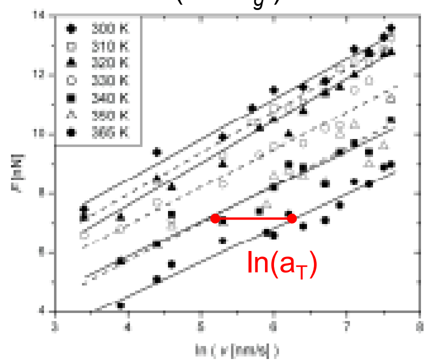
What is the origin for the kink in F(L) isotherms of PS at $L = L^*$?

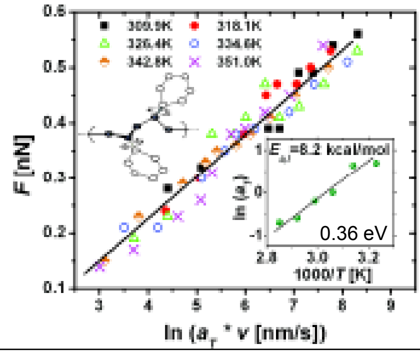
Knorr, Gray and Overney, *J. Chem. Phys.*, **129**, 074504 (2008).

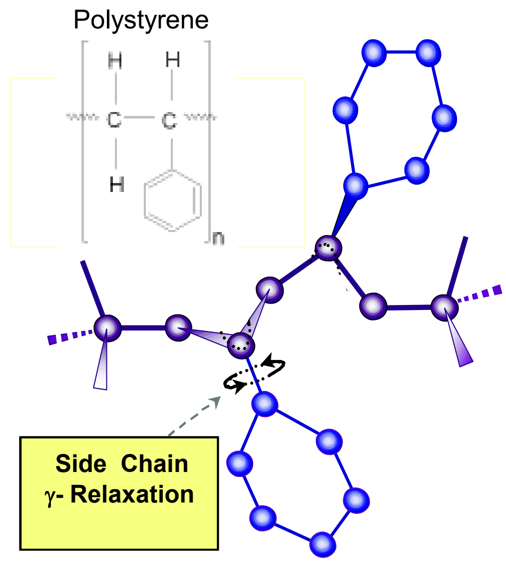
Superposition Principle: Intrinsic Friction Analysis (IFA)

$L < L^*$ ($T < T_g$)

S. Sills and R.M. Overney, (2003), *Phys. Rev. Lett.* 91(9), 095501, 2003.







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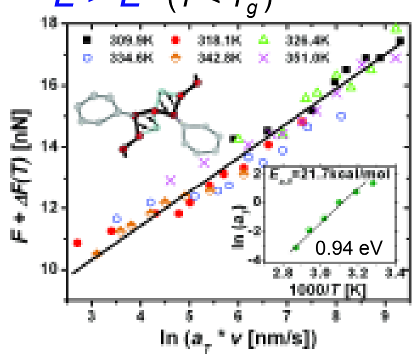
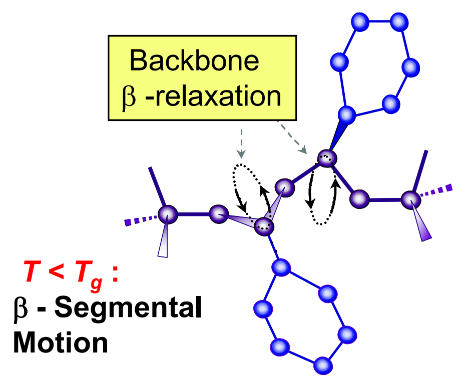
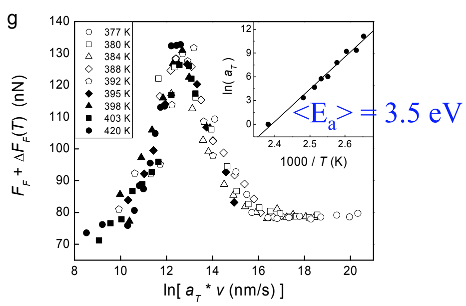


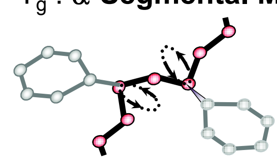


Knorr, Gray and Overney, *J. Chem. Phys.*, **129**, 074504 (2008).

Above T_g

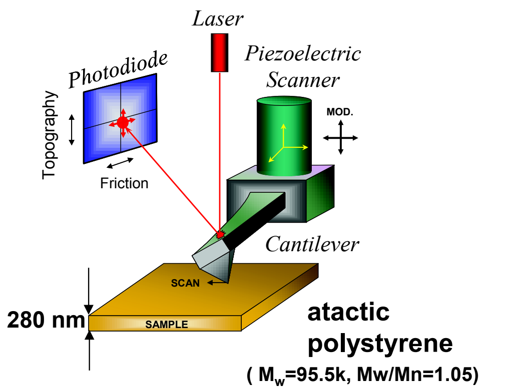


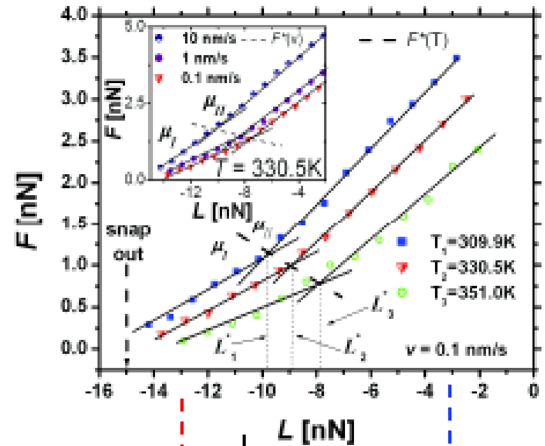
$T > T_g$: **α-Segmental Motion**

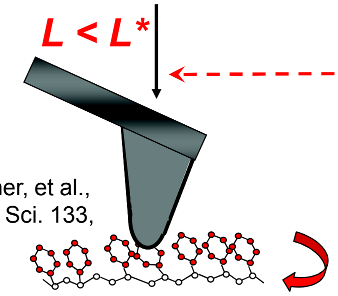


S.E. Sills, T. Gray, R.M. Overney, Chem. Phys. Lett. **123**, 134902, (2005).

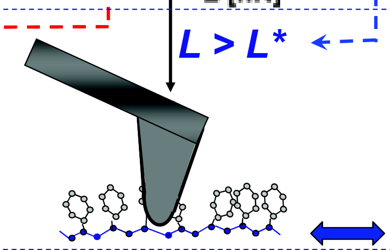
Tribology: Molecular Dissipation Mechanisms







D. A. Fischer, et al., Appl. Surf. Sci. 133, 58 (1998).



Phenyl loading capacity: (9.9 ± 1 kcal/mol)
(0.4 eV)

Knorr, Gray and Overney, *J. Chem. Phys.*, **129**, 074504 (2008).

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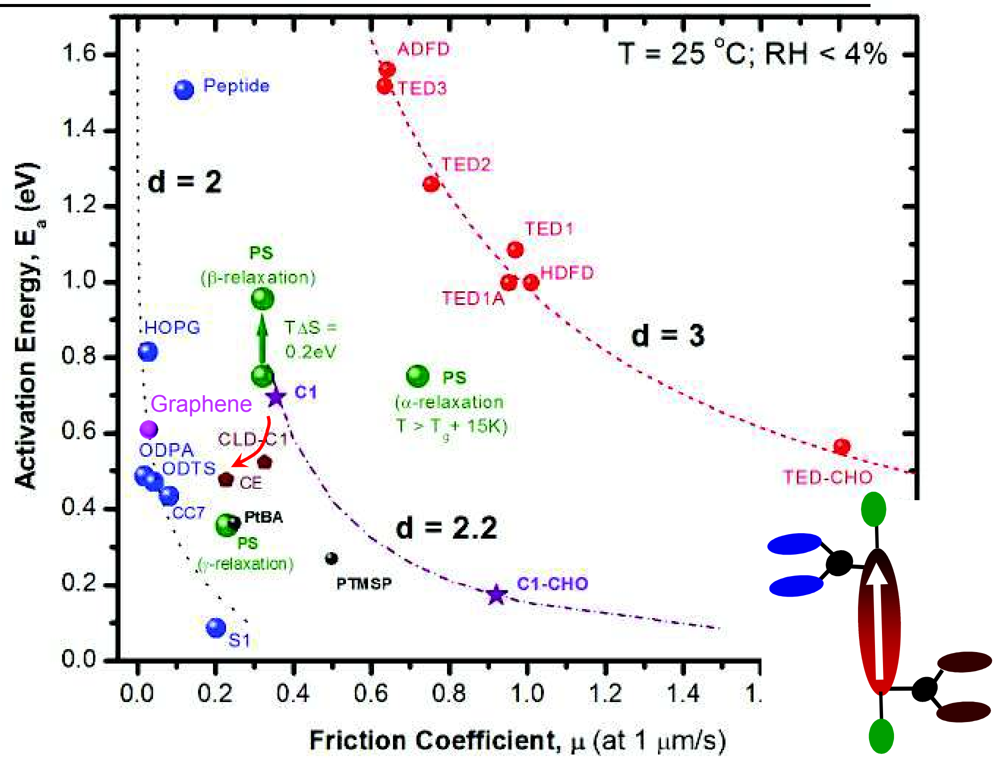
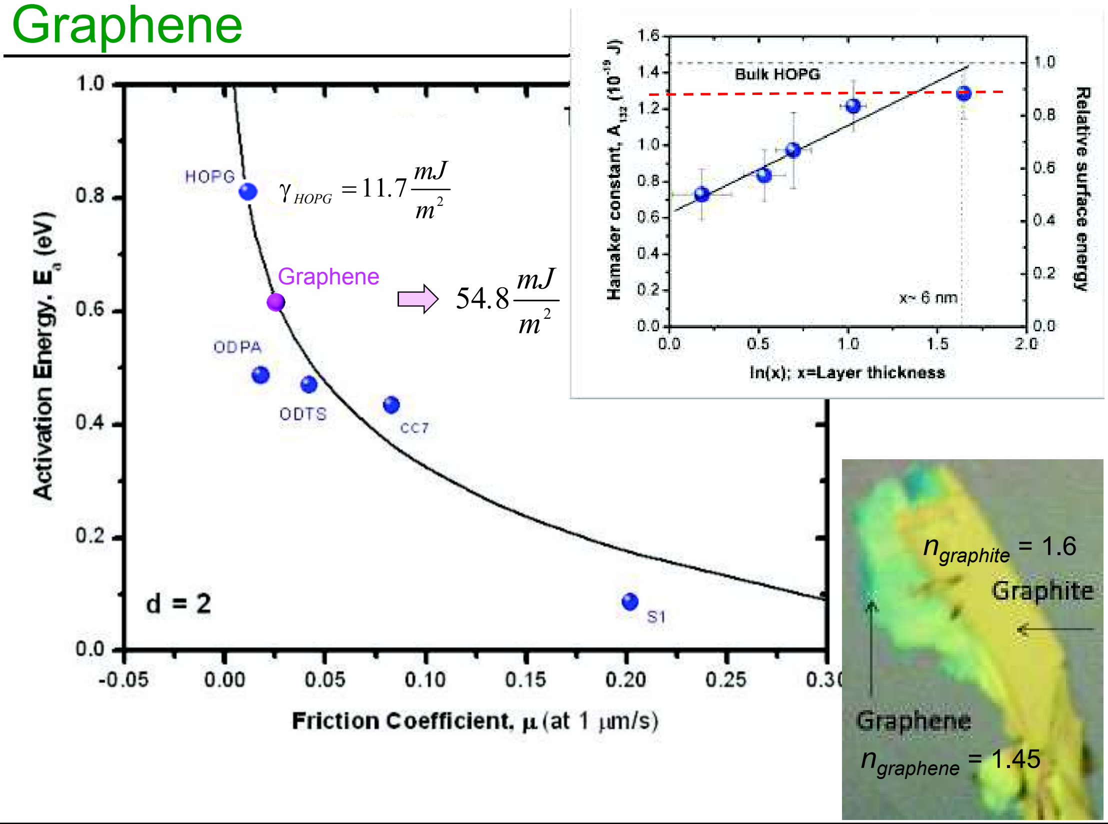
R.M. Overney University of Washington

Energy – Friction Coefficient Relation?



Graphene


1.0
0.8
0.6
0.4
0.2
0.0
-0.05
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Activation Energy, E_a (eV)
Friction Coefficient, μ (at 1 μm/s)
HOPG
$\gamma_{HOPG} = 11.7 \frac{mJ}{m^2}$
Graphene
$54.8 \frac{mJ}{m^2}$
ODPA
ODTS
CC7
S1
d = 2
Hamaker constant, A_{132} (10^{-19} J)
Relative surface energy
Bulk HOPG
x~ 6 nm
ln(x); x=Layer thickness
$n_{graphite}$ = 1.6
Graphite
Graphene
$n_{graphene}$ = 1.45