Molecular Friction Dissipation and Mode Coupling in Organic Monolayers and Polymer Films

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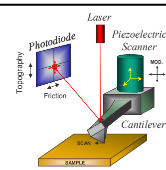
Content



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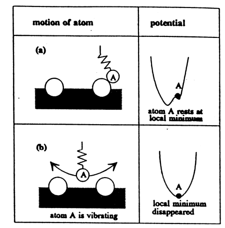
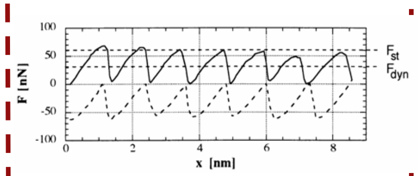
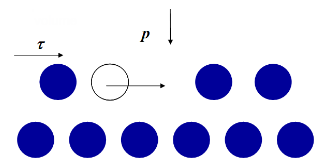
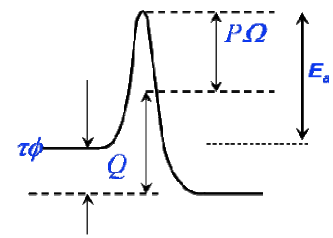
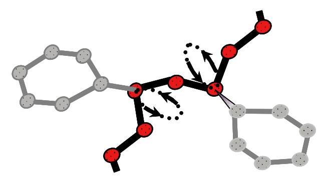
  → Stick Slip
- Friction as a Simple Activated Process
  → Eyring Analysis
- Friction and Thermal Mode Coupling (Material specific energy)
  → Time Temperature Superposition Analysis

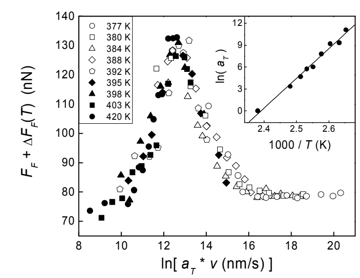




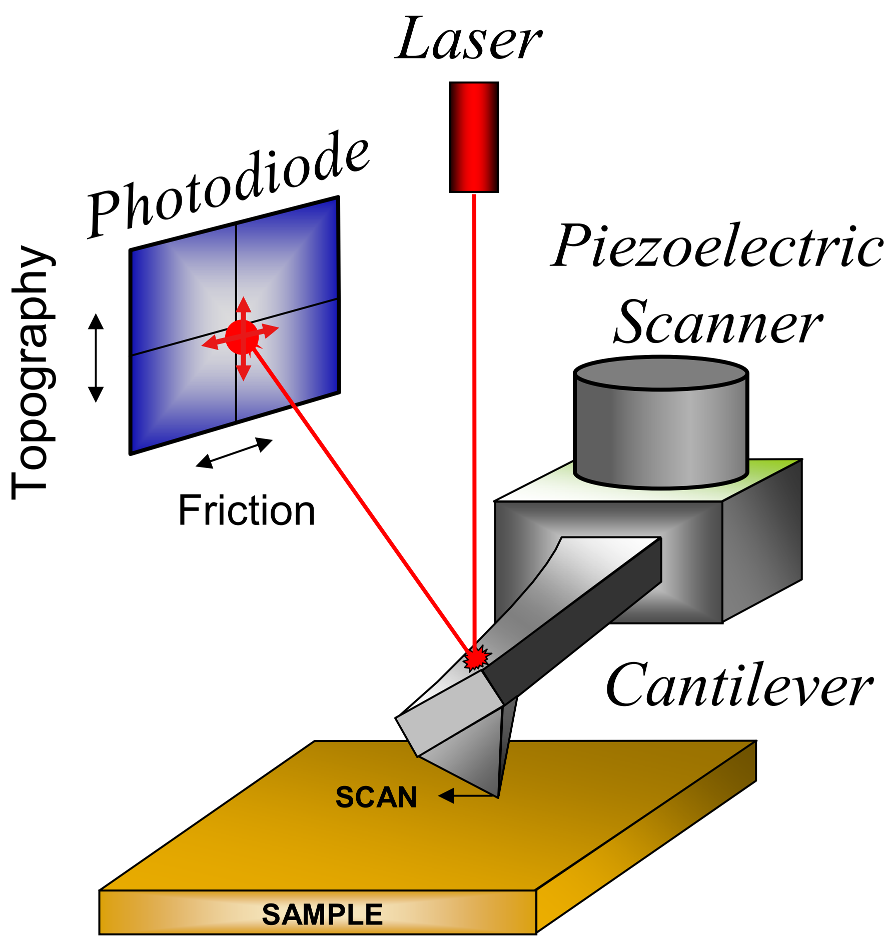


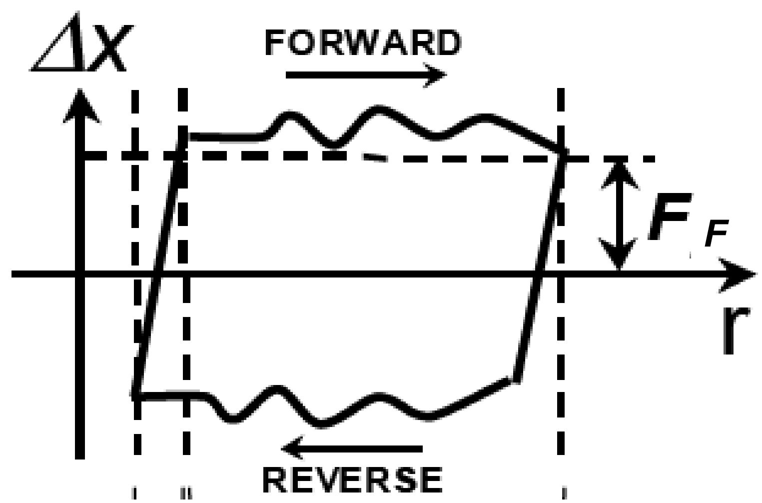






Lateral Force Microscopy





Nanoscale Friction on Crystalline Surfaces

Molecular Stick-Slip Model

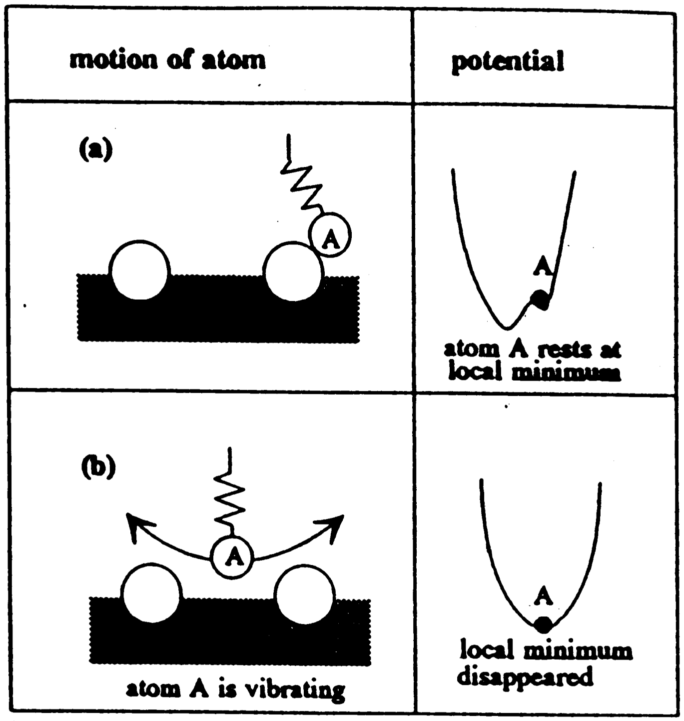
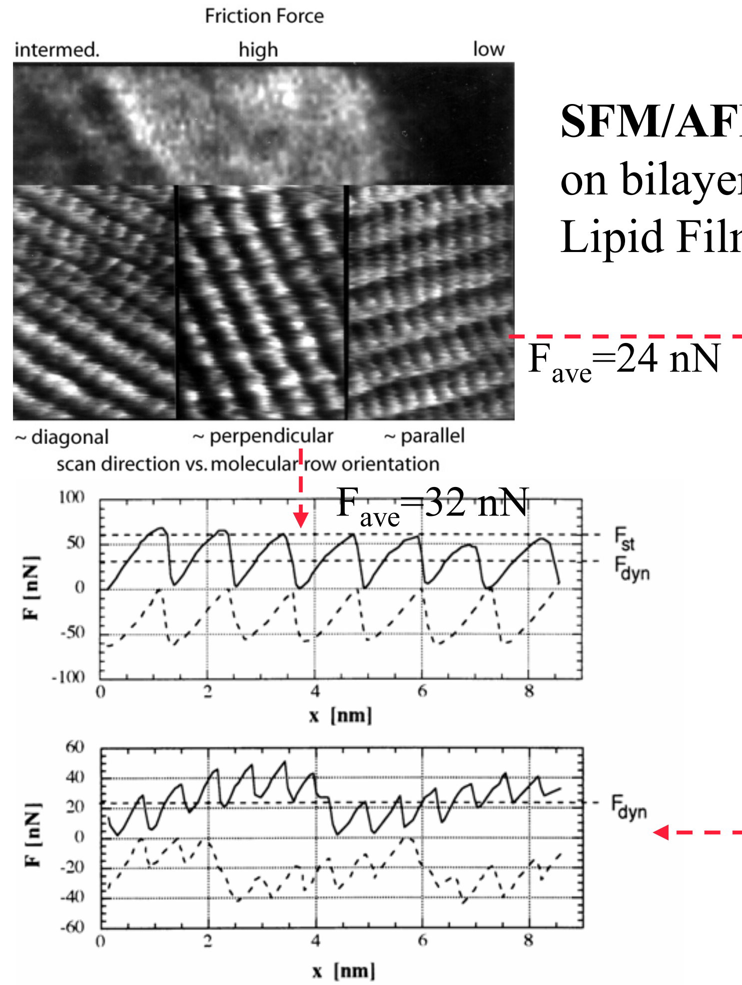


Fig. 1.15: Motion in the independent oscillator model.

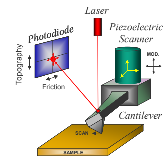
Prandtl- Tomlinson
Model



SFM/AFM
on bilayer
Lipid Film

R. M. Overney et al., Phys. Rev. Lett. **72**, 3546 (1994)

➔ observed single molecular jump occurrences below 100 nm/s, and stochastic multiple jump occurrences above 800 nm/s



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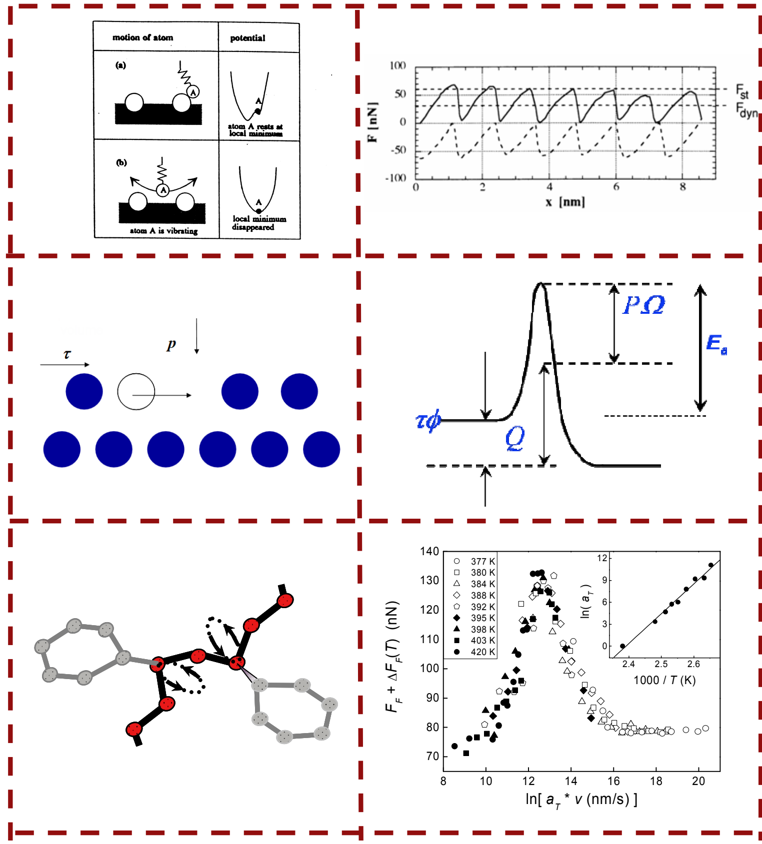


The Eyring Model

"Reaction" rates:

$$k_v \propto \exp\left(\frac{-Q}{kT}\right)$$; Q … intrinsic barrier

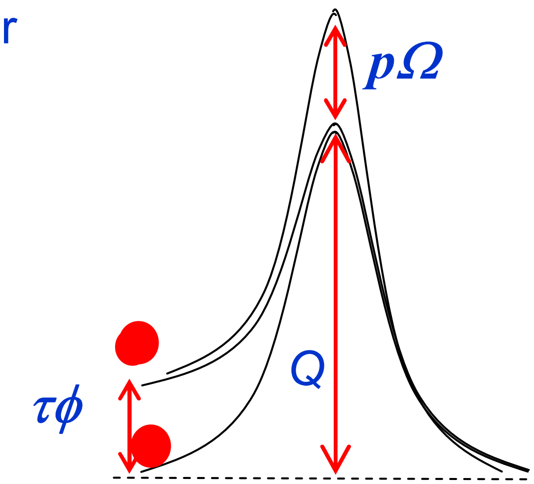
$$k_v \propto \exp\left(\frac{-Q+\phi\tau}{kT}\right)$$; τ …shear stress

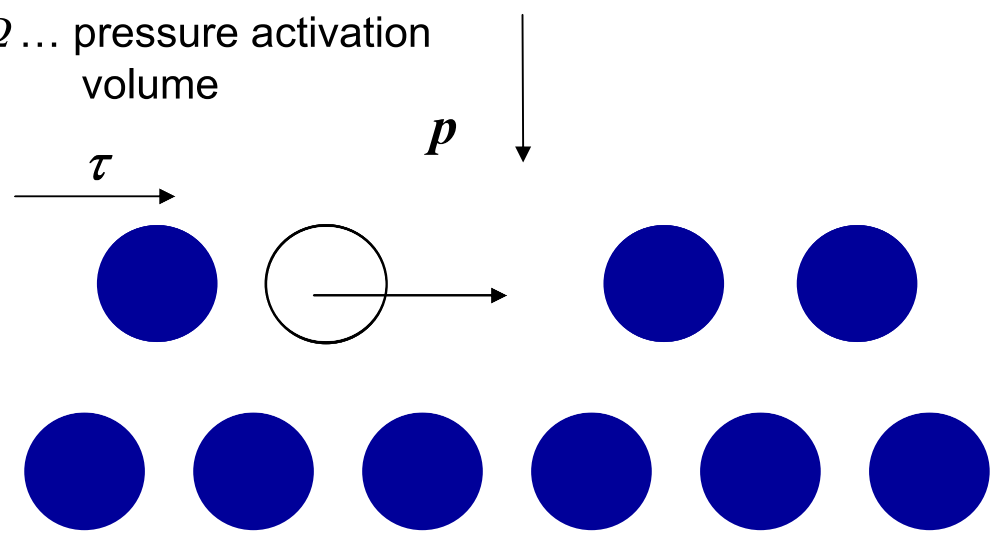
ϕ … stress activation volume

$$k_v \propto \exp\left(\frac{-Q-p\Omega+\phi\tau}{kT}\right)$$; p …pressure

Ω … pressure activation volume

Effective Energy Barrier:





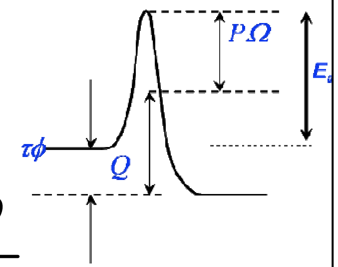
Eyring, *J. Chem. Phys*. **3**, 107, (1935).
Eyring, *J. Chem. Phys*. **4**, 283, (1936).
Duckett, Rabinowitz, and Ward, *J. Mat. Sci*. **5**, 909 (1970).

The Eyring Model: Friction (in high stress limit)

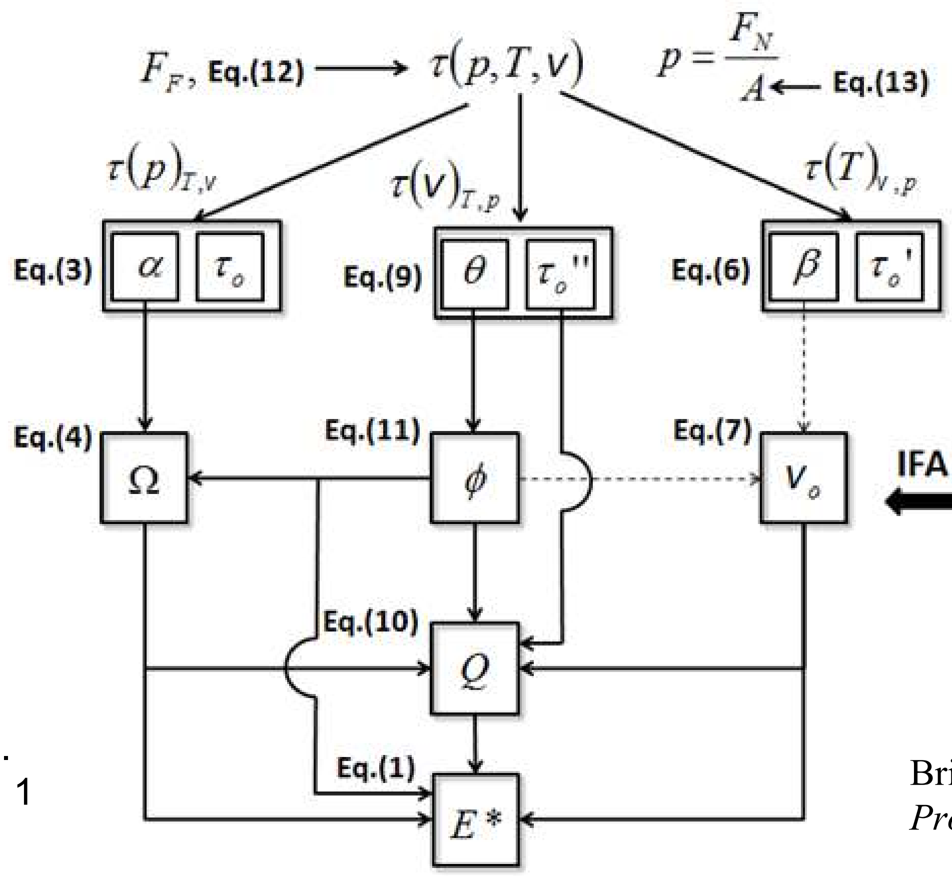
$$v = v_o \exp\left(\frac{-E_a}{kT}\right)$$

$$E_a = Q + p\Omega - \tau\phi$$

$$\ln\left(\frac{v}{v_0}\right) = \frac{-Q}{kT} - \frac{p\Omega}{kT} + \frac{\tau\phi}{kT}$$



v = velocity; v_o = system specific velocity



$$\tau = \theta \ln v + \tau_o''$$

$$\tau = \alpha p + \tau_o'$$

$$\tau = -\beta T + \tau_o'''$$

$$\phi = \frac{kT}{\theta}$$

$$\Omega = \alpha\phi$$

Knorr, Overney et al.
J. Chem. Phys. **134**, 1
04502 (2011)

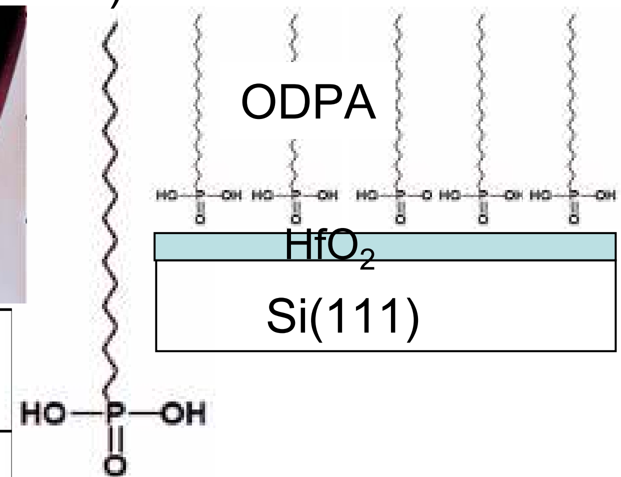
Briscoe and Evans,
Proc. R. Soc. A. **380**, 389 (1982).

Eyring Analysis of ODPA and ODTS†

Material: C_{18} Monolayer of octadecyl-phophonic acid (ODPA) reacted via surface hydroxyls on HfO_2, supported by Si(100).

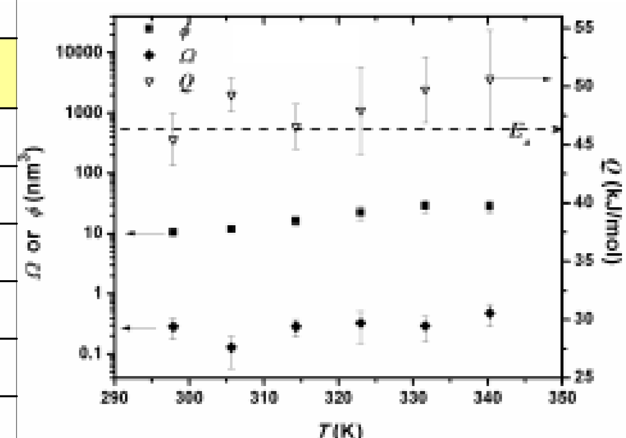
Analysis: Using smooth SFM tips with up to 400 nm tip radii.

† K. Subhalakshmi, S. K. Biswas et al., Trib. Lett., **32**, 1 (2008)



Eyring Parameters	ODPA (R ~20 nm)	ODPA (R ~400 nm)	ODTS † (R~30nm)
T, K	297	297	295
L, nN	41.9	240	46.5
A ($\times 10^{-16}$) m^2	2.33	192	5.22
p, MPa	180	13	89
α (at 1µm/s)	0.018	0.020	0.042
ϕ, nm^3	2.10	13.06	4.69
Ω, nm^3 (at 1µm/s)	0.037	0.255	0.1972
$\zeta=\phi/\Omega$	56±6	51±6	24
$\tau\phi$, kJ/mol	3.5	5.0	14.5395
$p\Omega$, kJ/mol	2.8	1.9	10.5824
Q, kJ/mol (eV)	46.3 (0.48)	48.3 (0.50)	45.05 (0.47)
E^*, kJ/mol (eV)	46±6 (0.47±0.06)	45±5 (0.47±0.05)	41.09 (0.43)

$$E_a = Q + p\Omega - \tau\phi$$



Knorr, Overney et al. J. Chem. Phys. **134**, 104502 (2011)

Eyring Analysis of PtBA

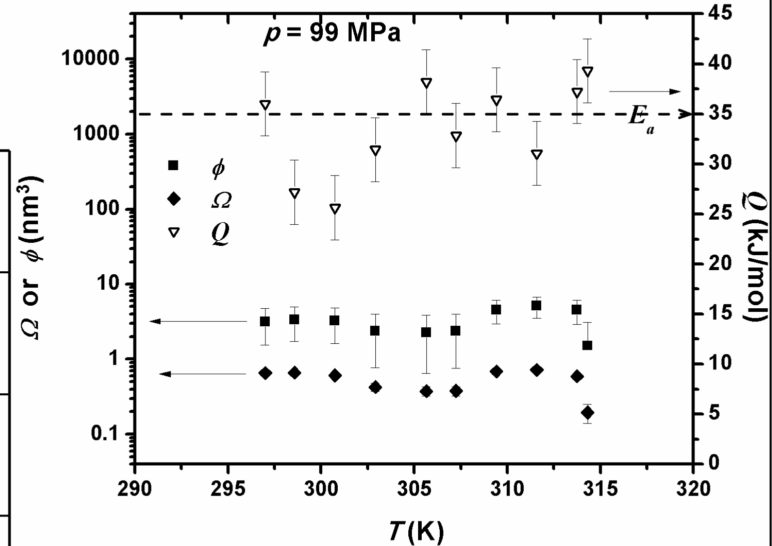
Material: Poly(tert-butyl acrylate) (PtBA) MW 100k, 200 nm thick spin coated film on Si(111)

Analysis: Using smooth SFM tips with up to 400 nm tip radii.

Eyring Parameters	PtBA (T = 315 K < T_g)	ODPA (T = 297 K)
E^*, kJ/mol (eV)	30±3 (0.31)	46±6 (0.47±0.06)
Q, kJ/mol (eV)	35-43 (0.36-0.45)	46-48 (0.48-0.50)
$\zeta=\phi/\Omega$	7.8	51-56
v_o, m/s	~ 0.1	~ 100

ζ … dimensionless deformation ratio

v_o ... system/process characteristic velocity



$$E_a = Q + p\Omega - \tau\phi$$

Based on Eyring's Cage Model:

$$v_o = Cvb$$

C … *coupling constant* [0,1]
ν … jump attempt frequency
b … jump {barrier }distance

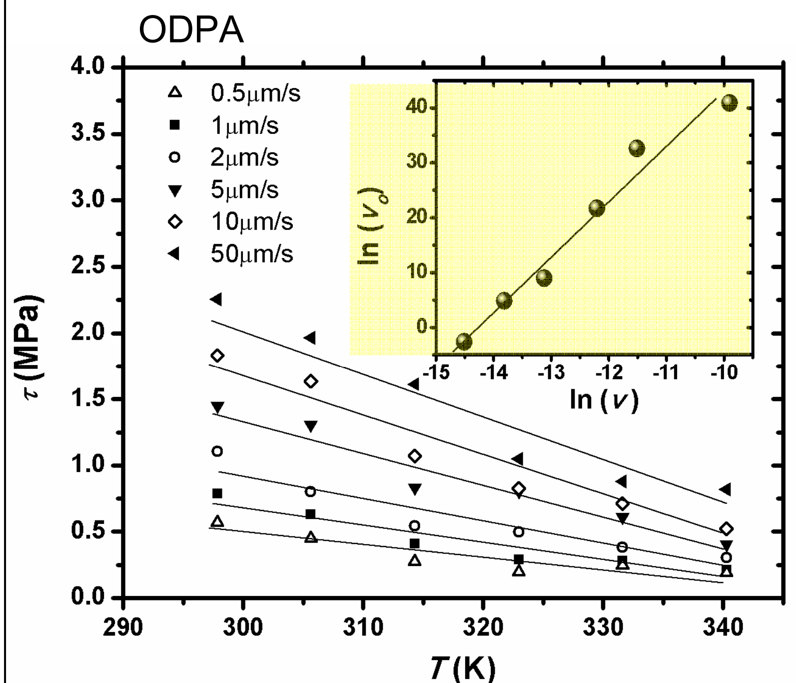
v_o reflects the system's molecular ability to relax via the "jump velocity" νb.

as Q = f(v_o), v_o is critical.

b < 1.5 nm based on IFA for PtBA (T < T_g)

Knorr, Overney et al., J. Chem. Phys. **134**, 104502 (2011)

Eyring Analysis: v_o

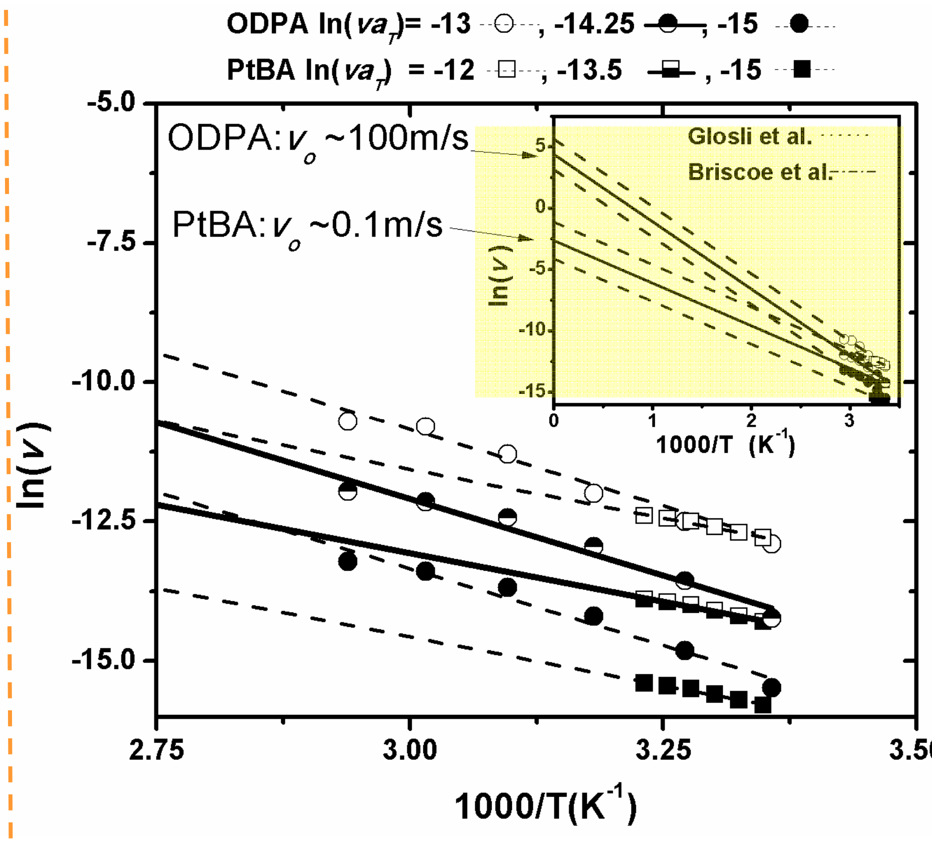


Using the Eyring Analysis, i.e.,

$$\tau = \tau_o'' + \theta \ln v;\ \ \tau_o'' = \frac{Q + p\Omega - kT \ln v_o}{\phi}$$

➔ large spread in v_o (to part unphysical)

$$v_o \in \left[10^{-2} - 10^{17}\right]$$



Using Intrinsic Friction Analysis (IFA) assuming $Q \gg p\Omega - \tau\Phi$

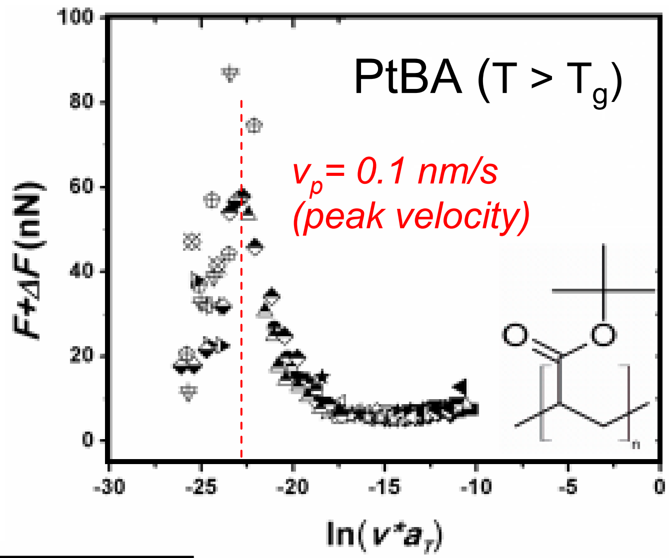
➔ v_o could be estimated

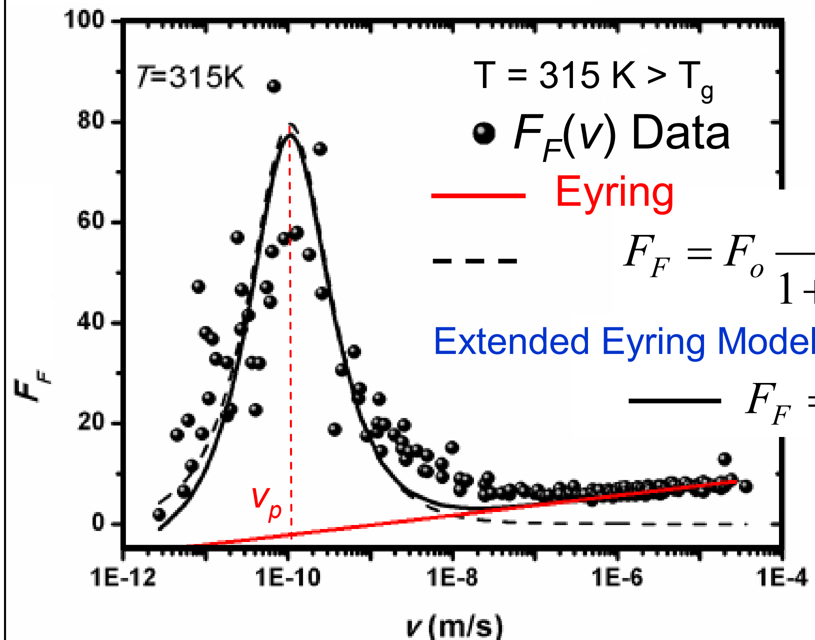
$$V_o = \begin{cases} \sim 100 \text{ m/s for ODPA} \\ \sim 0.1 \text{ m/s for PtBA } (T < T_g) \end{cases}$$

Knorr, Overney et al. J. Chem. Phys. **134**, 104502 (2011)

Other Shortcoming of Eyring Analysis

Peaks in friction-velocity curves lead to unphysical behavior of the activation volumes.
Reason: Eyring analysis lacks intrinsic relaxation rates.

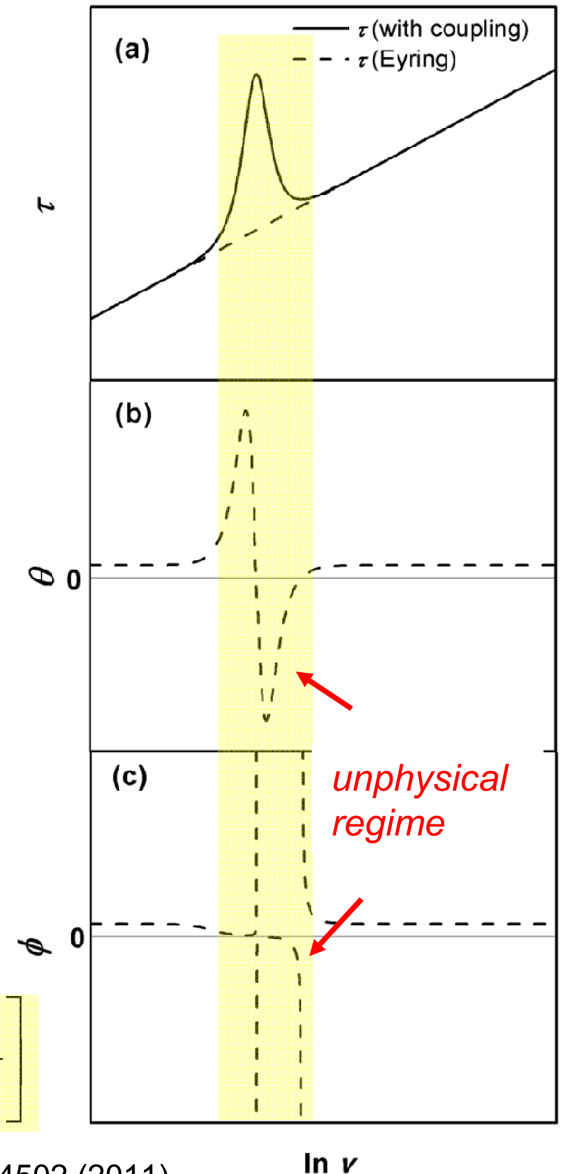




$$F_F = F_o \frac{De}{1+De^2}; De = \frac{t_t}{t_c} = \frac{v}{v_p}$$

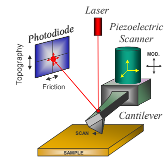
Extended Eyring Model

$$F_F = \left[F_o \frac{De}{1+De^2} \right] + \left[\frac{kT}{\phi'} ln \frac{v}{v_o} + \frac{Q}{\phi'} + \frac{p\Omega}{\phi'} \right]$$



Knorr, Overney et al. J. Chem. Phys. **134**, 104502 (2011)

Content



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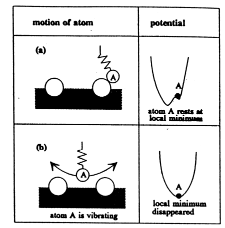
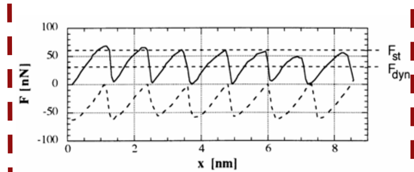
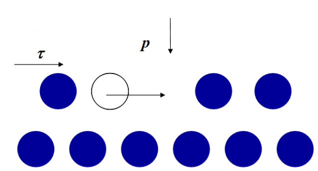
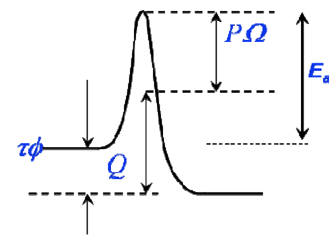
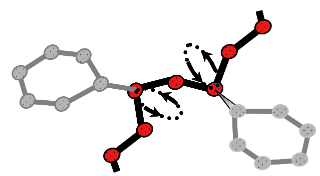
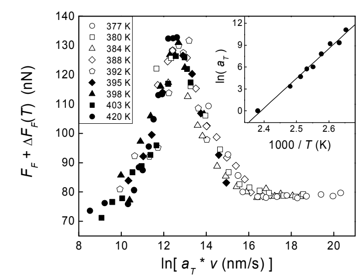






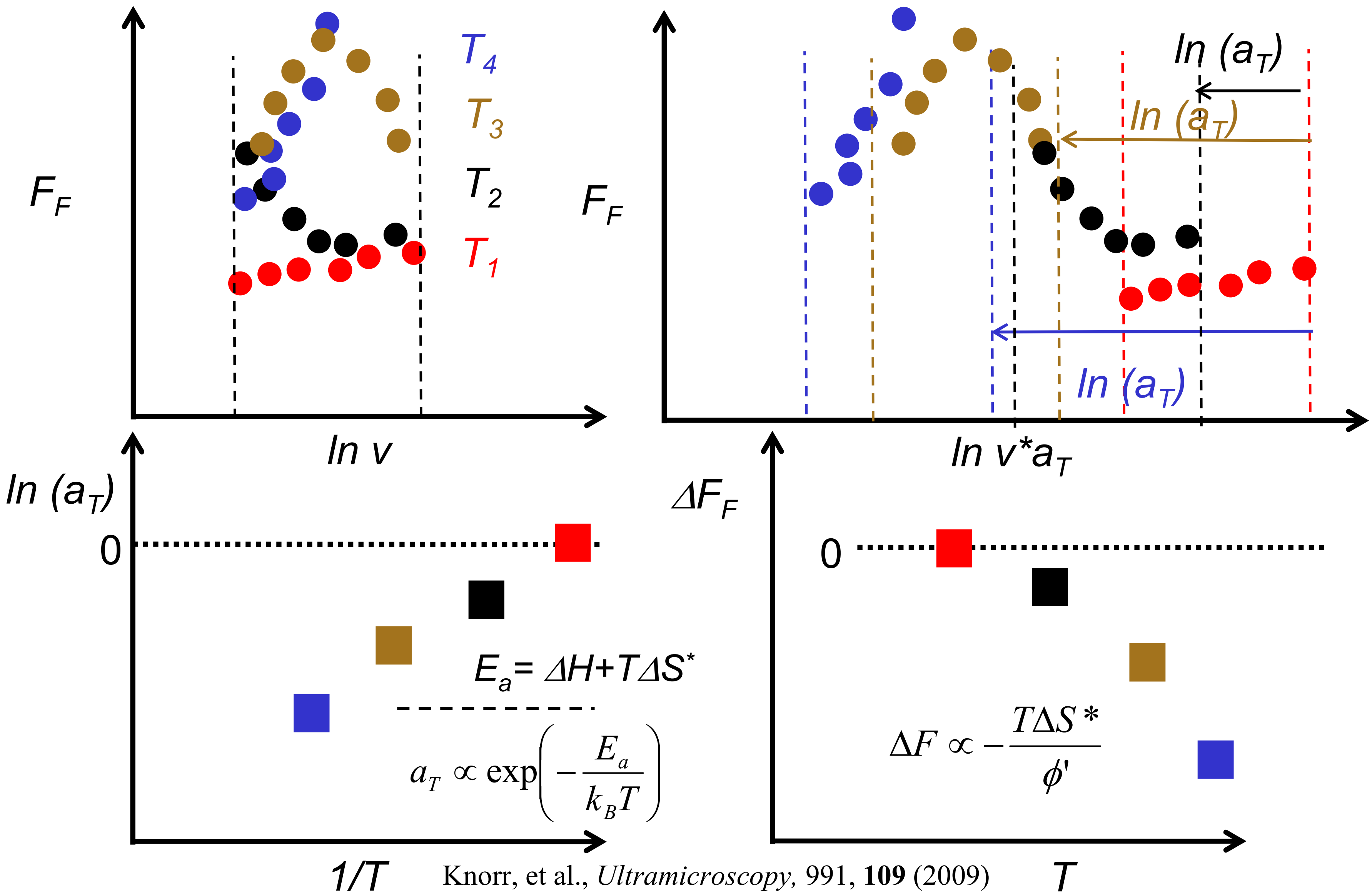






Time-Temperature Superposition - Intrinsic Friction Analysis (IFA)

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



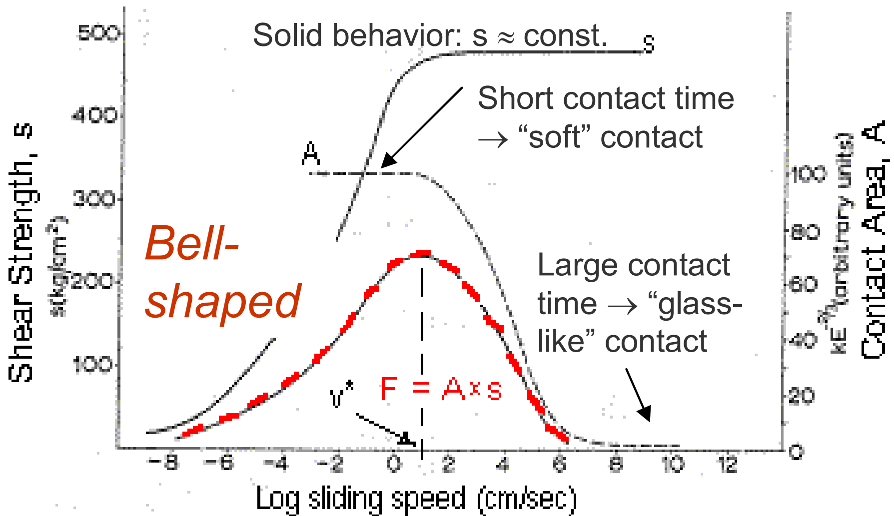
Knorr, et al., *Ultramicroscopy,* 991, **109** (2009)

Adhesive-Viscoelastic Concept of Friction

Spherical slider on amorphous polymer rubber melt

(Ludema and Tabor, Wear **9**, 329 (1966))

Acrylonitrile Butadiene for **T > T$_g$**



Adhesive model: F = A × s

A … contact area, $A \propto E^{2/3}$

s … shear strength,

(a high frequency process in thin film)

F … Friction

ν^*/ν_c ~ 5-10 nm (molecular segment)

ν_c frequency corresponding to visco-elastic loss peak.

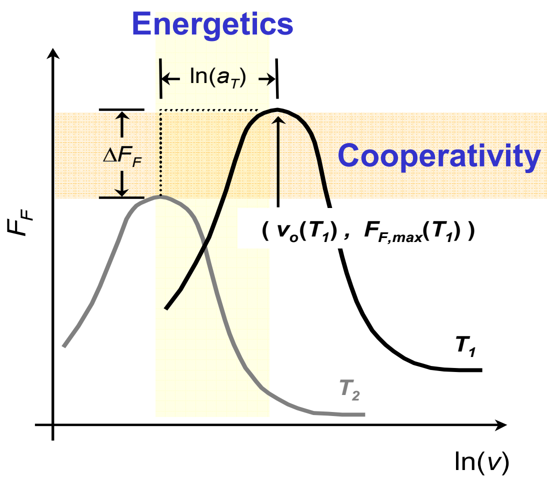
Conclusion of Ludema and Tabor, (also K.A. Grosch., Proc. R. Soc., London (1963) **274**, 21):

Rubber friction is a combination force involving surface and bulk effects. The "bulk effects" involve chain segmental slips during the sliding process.

-> *Molecular Deformation Concept* (*Intrinsic Friction Concept*)

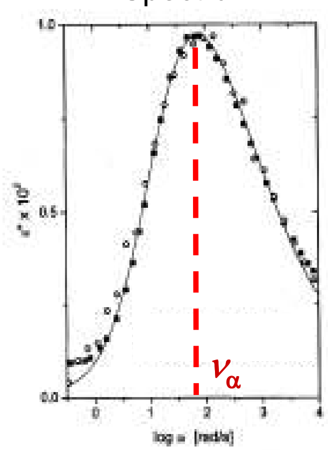
Nanoscopic Analysis of the Glass Forming Process

Intrinsic Friction Analysis (IFM)

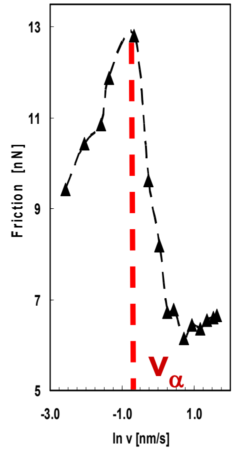


Combined with dielectric spectroscopy, the friction analysis provides the temperature resolved length scale of cooperative motion. The cooperation lengths X_d compare qualitatively well with predictions based on MD simulations and previous time-based experiments using model assumptions to deduce length scale information.

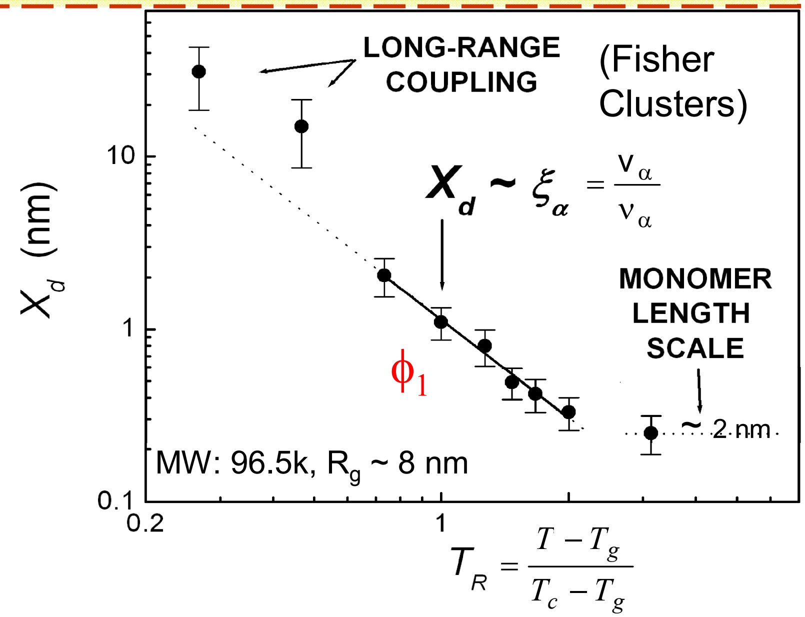
Dielectric Frequency Spectrum



Friction Velocity Spectrum



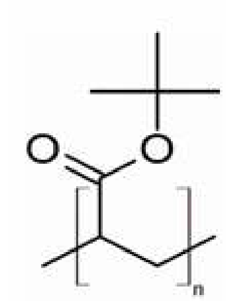
$$X_d = \frac{v_\alpha}{V_\alpha}$$

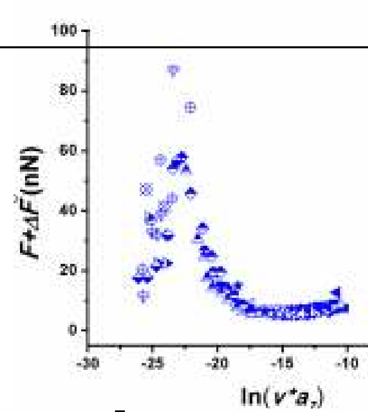


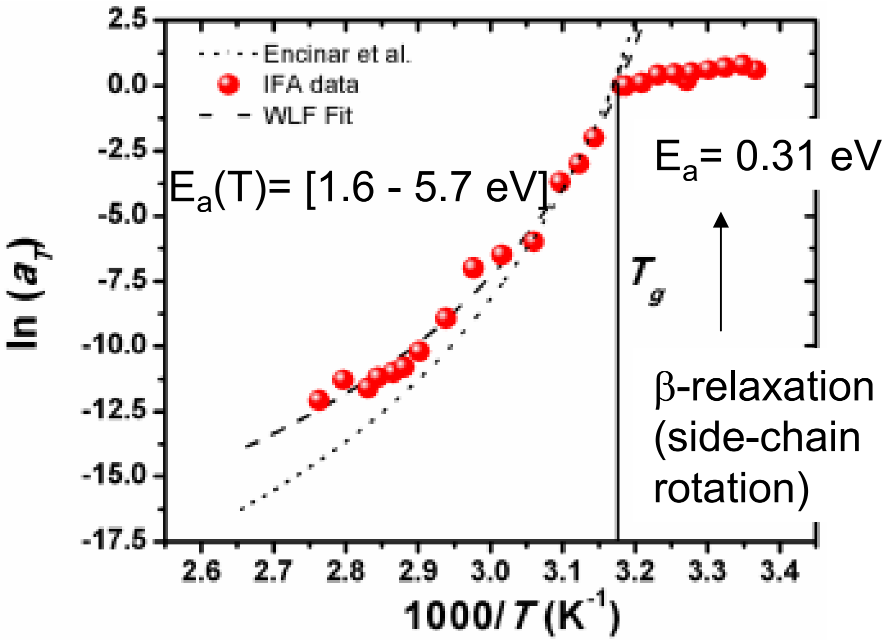
S.E. Sills, … R.M. Overney, Chem. Phys. Lett. **123**, 134902, (2005)

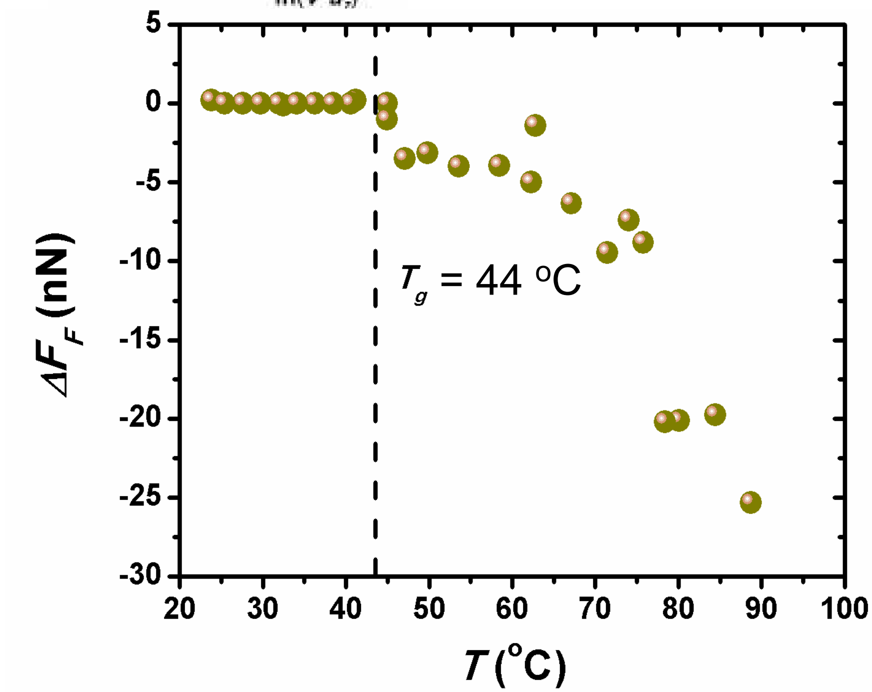
IFA on PtBA:

Poly(tert-butyl acrylate)









Williams-Landel-Ferry:

$$\log_{10} a_T = \frac{-C_1\left(T - T_o\right)}{C_2 + \left(T - T_o\right)}$$

	Encinar et al.	This work
T_o (K)	315.4	314.4
C_1	10.8	10
C_2	45.3	40.2

Knorr, Overney et al. J. Chem. Phys. **134**, 104502 (2011)

Encinar et al., *Polymer, 5650* **49** (2008)

IFA and Eyring Analysis

IFA and Eyring Parameters	ODPA (T=297K)	PtBA	
		T =315K < T_g	$T > T_g$
ΔH^* kJ/mol	48±5	35±4	54-75
$T\Delta S^*$, kJ/mol	~0	~0	100 – 490
$E_a = \Delta H + T\Delta S$, kJ/mol	**48±5**	**35±4**	~150 – 550
v_o, m/s (characteristic velocity)	~100	~0.1	-
v_p, m/s (peak velocity at T ≈ T_g)	-	-	0.1 nm/s
Q, kJ/mol (eV)	**46-48** (0.48-0.50)	**35-43** (0.36-0.45)	-
$E^* = Q + p\Omega - \tau\phi$, kJ/mol (eV)	46±6 (0.47±0.06)	30±3 (0.31)	-
ζ stress ratio	51-56	7.8	-

➔ $E_a \approx Q$ … (enthalpic) activation barrier

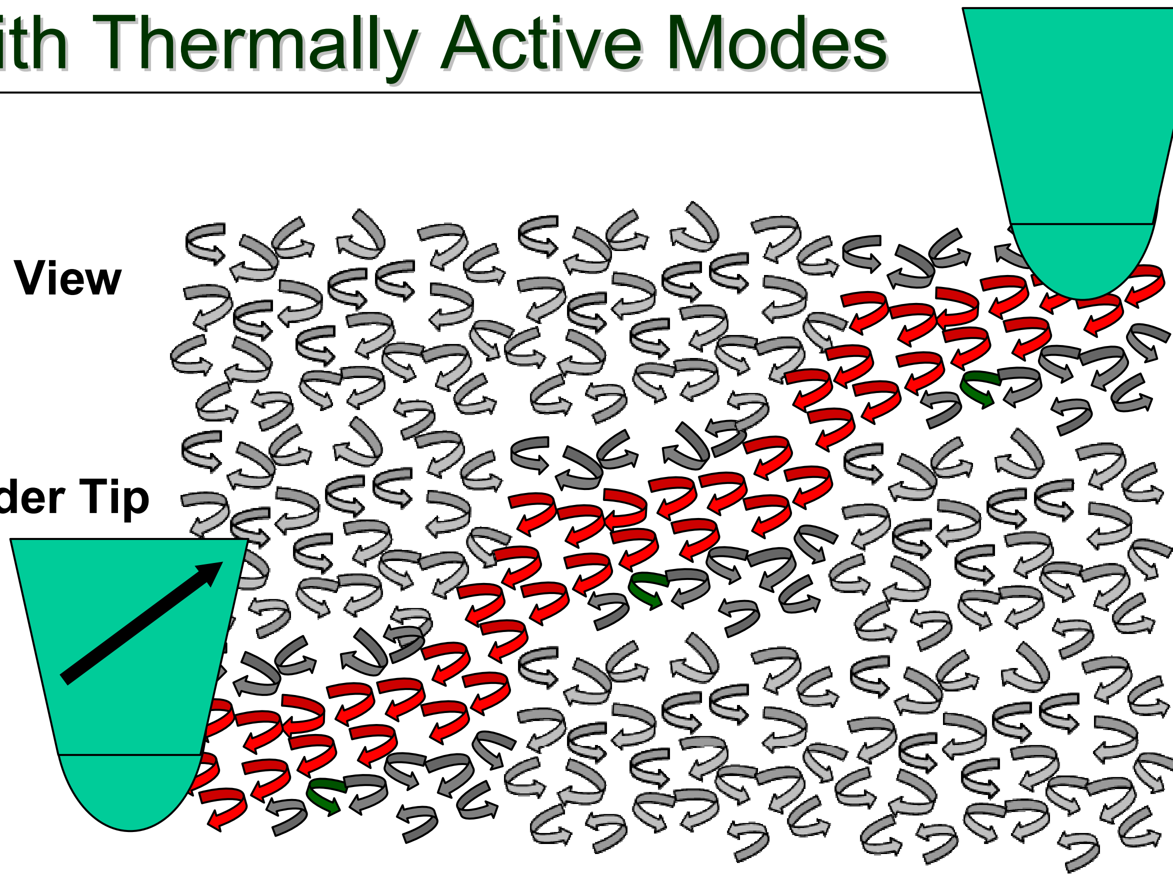
E* … effective barrier (contains also stress effects)

Knorr, Overney et al. J. Chem. Phys. **134**, 104502 (2011)

Coupling with Thermally Active Modes

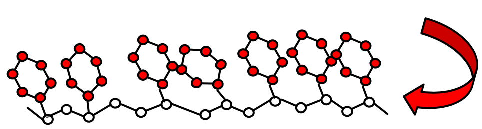
TOP View

Slider Tip



Slider 1D motion couples with thermally available mode(s) in sample

→ Energy Dissipative Process



SIDE View

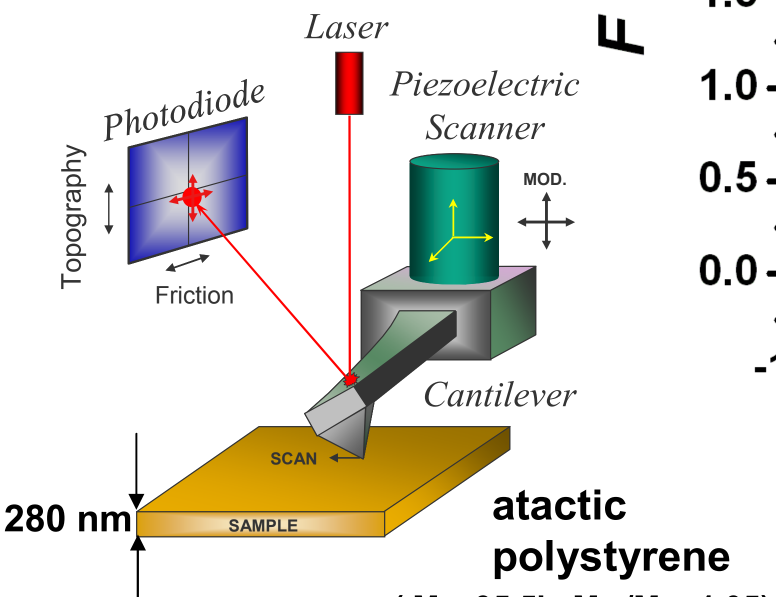
Thermally active modes

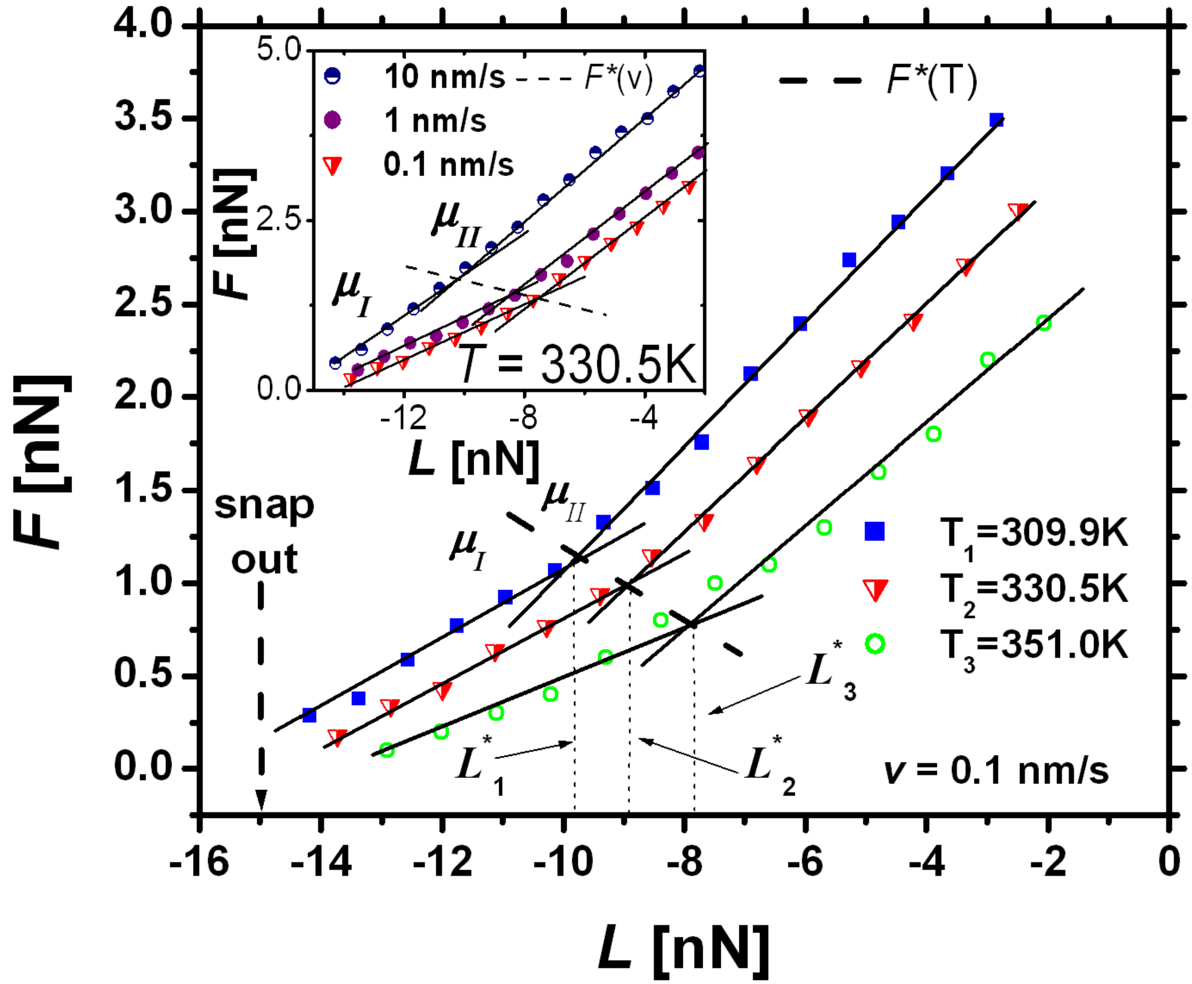
(rotational , translational, vibrational)

Frictional Dissipation: Load Distinctive Modes

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

Lateral Force
Microscopy





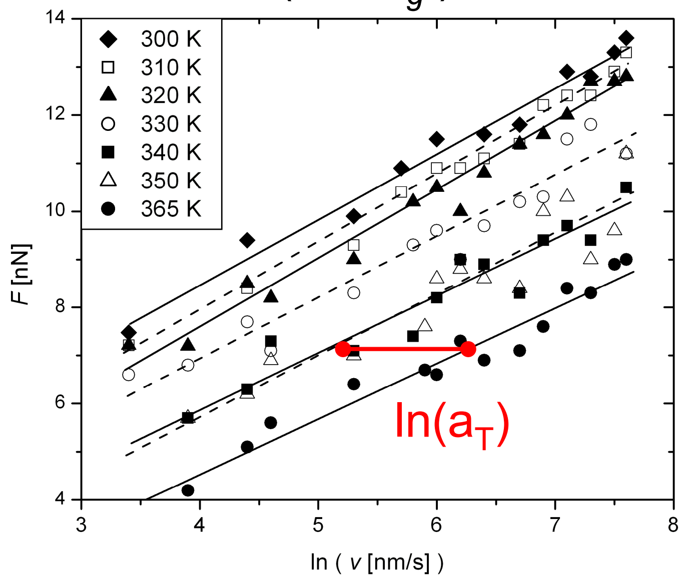
What is the origin for the kink in F(L) isotherms of PS at $L = L^*$?

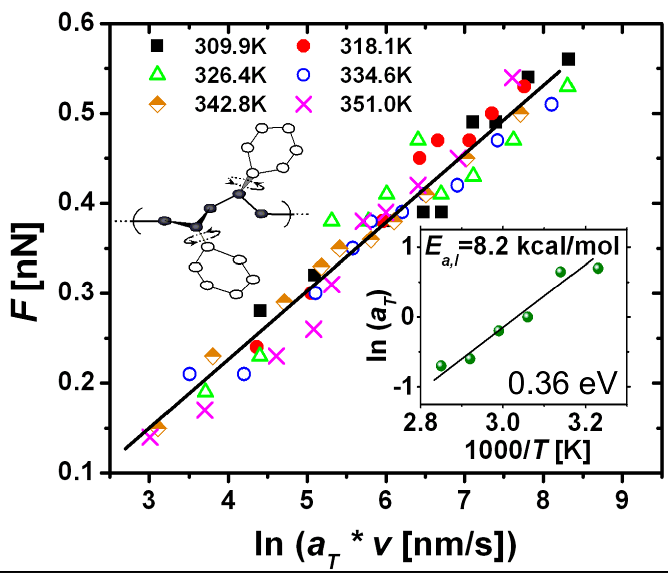
Knorr, Gray and Overney, *J. Chem. Phys.*, **129**, 074504 (2008).

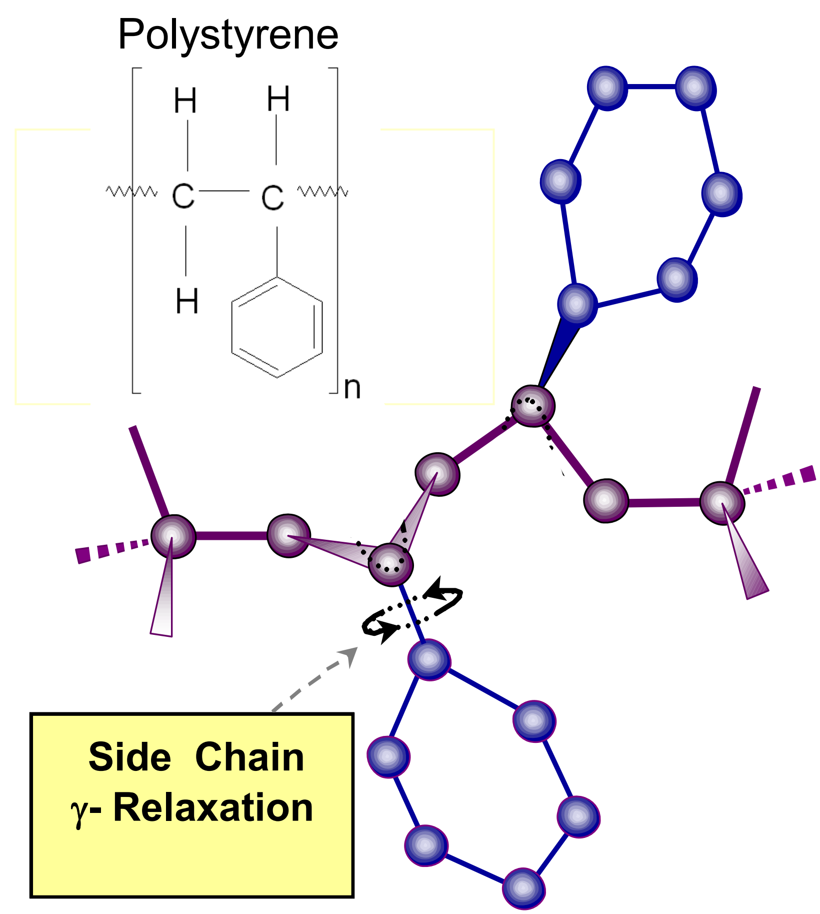
Superposition Principle: Intrinsic Friction Analysis (IFA)

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

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



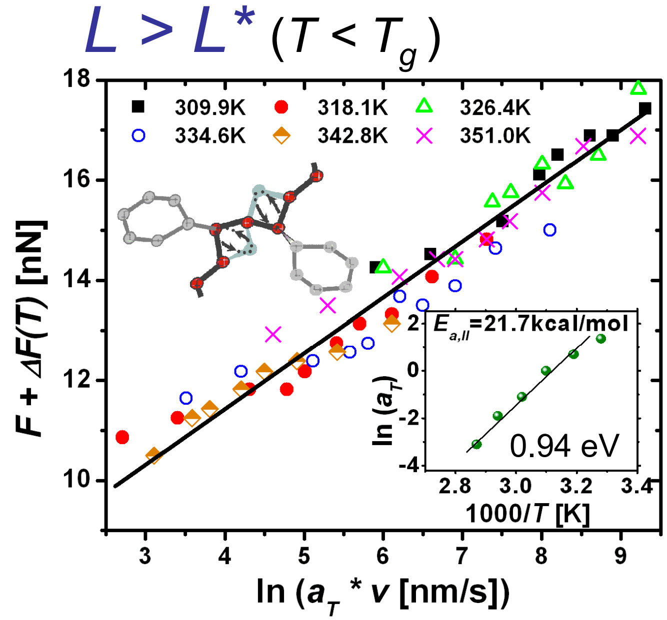


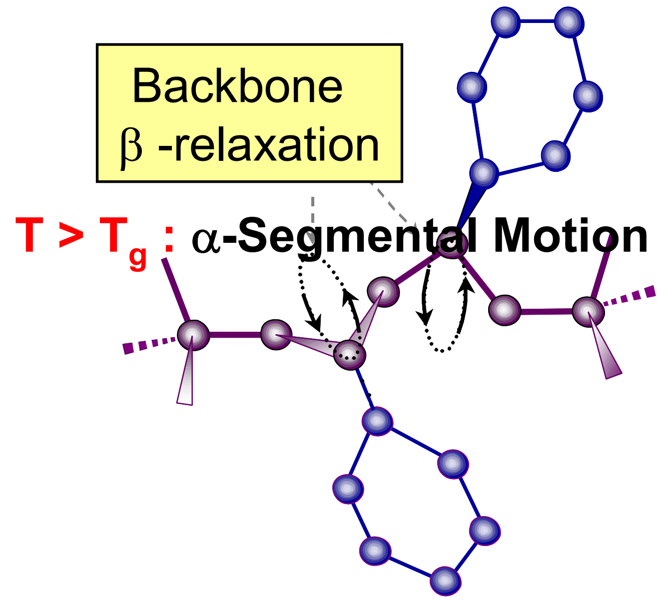


Knorr, Gray and Overney, *J. Chem. Phys.*, **129**, 074504 (2008).

Superposition Principle: Intrinsic Friction Analysis (IFA)

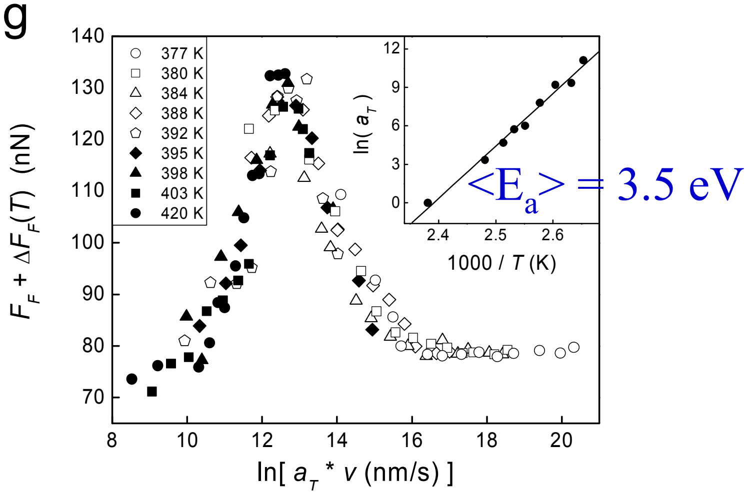
$L > L^*$ ($T < T_g$)

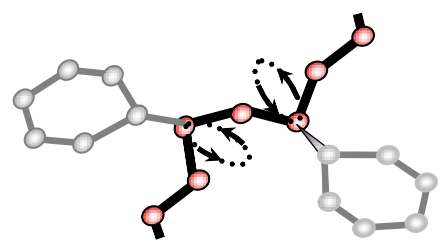




Knorr, Gray and Overney, *J. Chem. Phys.*, **129**, 074504 (2008).

Above Tg





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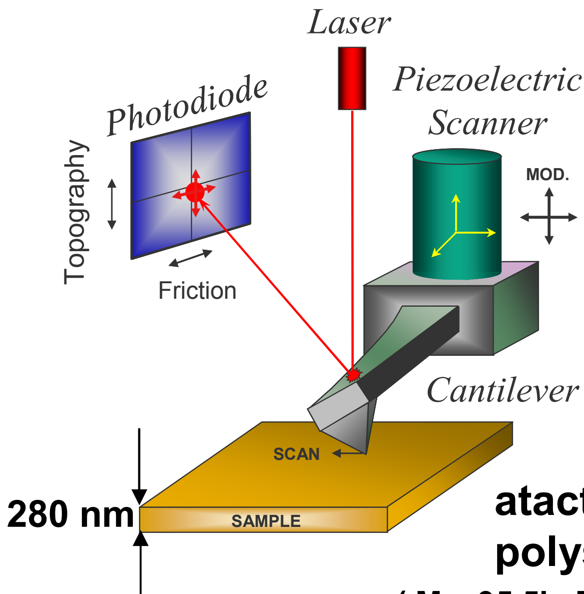
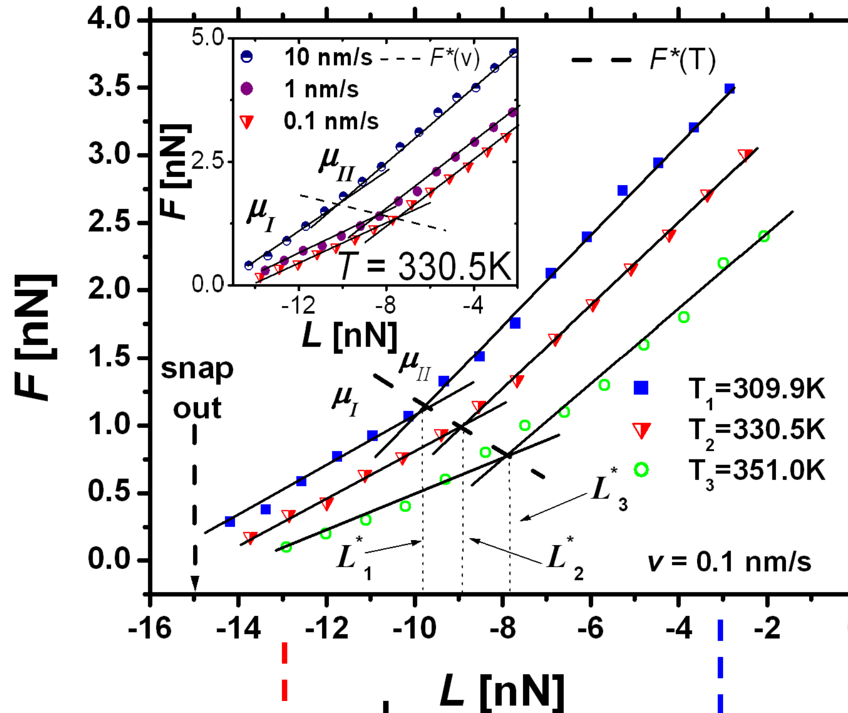
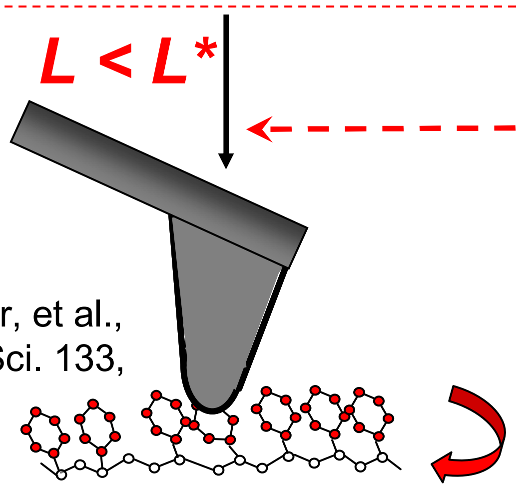
Tribology: Molecular Dissipation Mechanisms



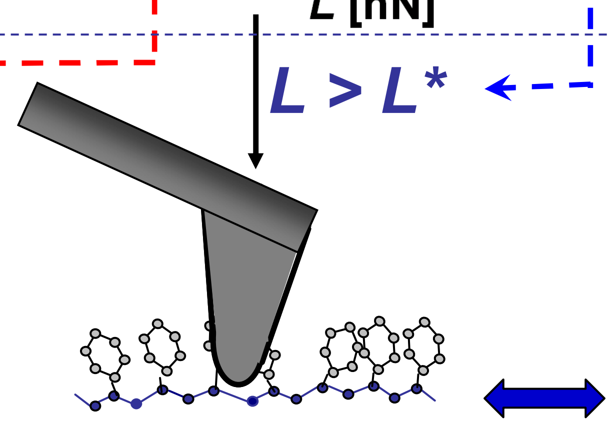
atactic polystyrene
(M_w=95.5k, Mw/Mn=1.05)



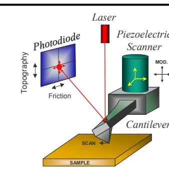


D. A. Fischer, et al., Appl. Surf. Sci. 133, 58 (1998).

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



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



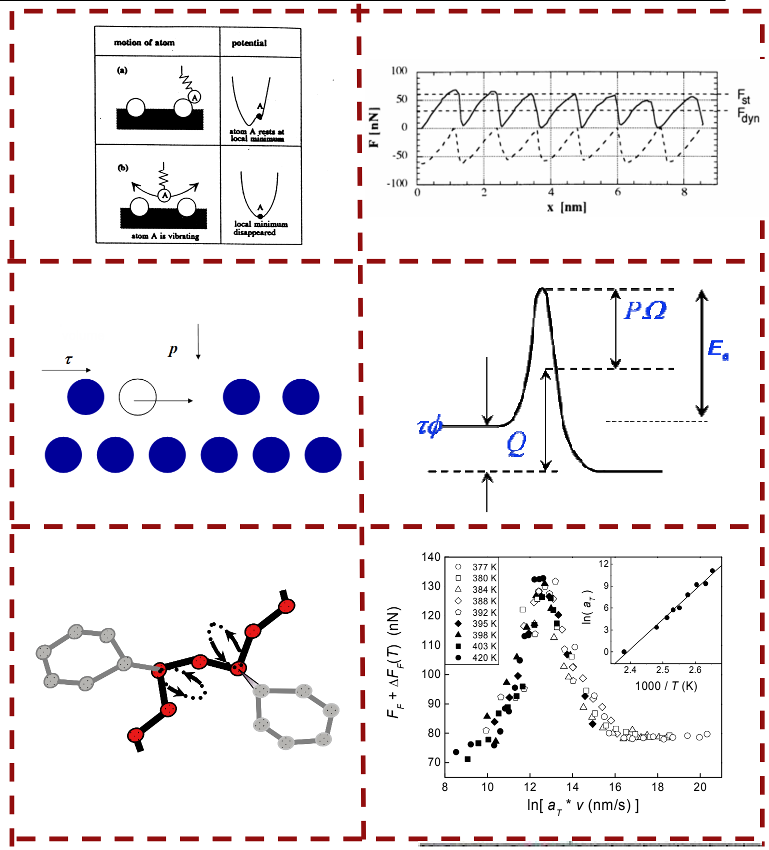
Summery

- Process Descriptive Analysis of Friction

  → Stick Slip
- Friction as a Simple Activated Process

  → Eyring Analysis
- Friction and Thermal Mode Coupling (Material specific energy)

  → Time Temperature Super-position Analysis



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