Theory of Nanoscale Friction

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Macroscopic vs. Nanoscale Friction

- Results from the interaction of hundreds of asperities on two rough surfaces
- Steady sliding after overcoming an initial static friction threshold
- Kinetic friction is approximately independent of the pulling velocity
  - $F_N \sim N$, $v \sim \text{m/s}$

- Interaction of a single asperity – the tip of an AFM – with an atomically flat surface
- Stick-slip motion of the AFM tip
- Friction force increases logarithmically with velocity
  - $F_N \sim nN$, $v \sim \mu\text{m/s}$
**Stick-slip motion at** $T = 0$

- **Potential energy:**
  \[ U(x, X) = u(x) + \kappa (x - X)^2/2, \]
  \[ u(x + a) = u(x) \]

- **Tip base position:** $X(t) = vt$

- **Friction force:** $f(X) = \kappa \left[ X - x_{\text{min}}(X) \right]$

- **Approximation of surface potential near inflection point** $x_0$: $f_0 = u'(x_0) = \max_x u'(x)$
  \[ u(x) = u(x_0) + f_0 (x - x_0) - \frac{u''(x_0)}{6} (x - x_0)^3 + ... \]

- **Barrier height:**
  \[ \Delta E(X) = U(x_{\text{max}}, X) - U(x_{\text{min}}, X) = \frac{4\sqrt{2}}{3 \sqrt{|u''(x_0)|}} (\kappa X_c X)^{3/2} \left( 1 - \frac{X}{X_c} \right)^{3/2} \]

- **Critical tip position:**
  \[ X_c = x_0 + \frac{\kappa}{2 |u''(x_0)|} + \frac{u'(x_0)}{\kappa} \]
Stick-slip motion at $T = 0$: arbitrary $\kappa$

- Friction force:

$$f(X) = f_0 - \frac{\kappa^2}{2 |u''(x_0)|}$$

$$+ \kappa \left( X - X_c + \sqrt{\frac{2\kappa(X_c - X)}{|u''(x_0)|}} \right)$$

- Force-dependent barrier height:

$$\Delta E_{\pm}(f) = \frac{4\sqrt{2}}{3} \frac{f_0^{3/2}}{\sqrt{|u''(x_0)|}} \left( \frac{\kappa}{\sqrt{2f_0 |u''(x_0)|}} \pm \sqrt{1 - \frac{f}{f_0}} \right)^3$$

Stick-slip motion at $T = 0$: small $\kappa$

- Potential energy:

$$U(x, X) = u(x) + \kappa(x - X)^2/2$$

$$\approx u(x) - f(X)x + \text{const}$$

- Friction force: $f(X) \approx \kappa X$

- Force-dependent barrier height:

$$\Delta E(f) \approx 4\sqrt{2} \frac{f_0^{3/2}}{3} \sqrt{\left| u'''(x_0) \right|} \left(1 - \frac{f}{f_0}\right)^{3/2}$$

\[Y. \text{ Sang, M. Dubé, and M. Grant, PRL 87 174301 (2001)}\]
Rate theory at small $\kappa$

Barrier height: $\Delta E(f) = \Delta E_0 (1 - f/f_0)^{3/2}$

Escape rate: $\omega(f) = \omega_0 \exp[-\Delta E(f)/k_B T]$

Elastic force: $f(t) = \kappa vt$

No-jump probability: $\dot{\pi}(t) = -\omega(f(t))\pi(t)$

In the force domain: $\kappa \pi'(f) = -\omega(f)\pi(f)$

Most probable slip force: $\pi''(f_m) = 0$

$\Rightarrow \kappa \omega'(f_m) = \omega^2(f_m)$

$\Rightarrow f_m \propto \left[\ln(v)\right]^{2/3}$

Rate equation modeling

- Probability to find the tip in the \( n \)th lattice site at time \( t \): \( p_n(t) \)

- Force in the \( n \)th stick phase
  \[ f_n(t) = \kappa(\nu t - na) ; \quad f_0(t) = \kappa \nu t \]

- Transition rates
  \[ \omega_n^\rightarrow(t) = \omega_n^\leftarrow(f_n(t)) ; \quad \omega^\rightarrow(f) = \omega^\leftarrow(-f) \]

- Rate equation
  \[ \dot{p}_n(t) = -\left(\omega_n^\rightarrow(t) + \omega_n^\leftarrow(t)\right)p_n(t) + \omega_{n-1}^\rightarrow(t)p_{n-1}(t) + \omega_{n+1}^\leftarrow(t)p_{n+1}(t) \]

- In the long-time limit
  \[ p_n(t) = p_{n-1}(t - a/\nu) = p_0(t - na/\nu) \]

- In the force domain:
  \[ p(f) := p_0(f / \kappa \nu) \]

\[ \kappa \nu p'(f) = -\left(\omega^\rightarrow(f) + \omega^\leftarrow(f)\right)p(f) + \omega^\rightarrow(f + \kappa a)p(f + \kappa a) + \omega^\leftarrow(f - \kappa a)p(f - \kappa a) \]

- Normalization
  \[ \sum_n p_n(t) = \sum_n p(f + n\kappa a) = 1 \Rightarrow \int_{-\infty}^{\infty} df \ p(f) = 1 \]
Regimes of stick-slip motion

\[ \kappa a \gg \left( \frac{d \ln \omega}{df} \right) ^{-1} \]

Logarithmic regime

\[ \kappa a \ll \left( \frac{d \ln \omega}{df} \right) ^{-1} \]

Linear response regime

\[ v \gg a \omega \rightarrow (\kappa a / 2) \]

Box-like \( p(f) \) \hspace{1cm} Bell-shaped \( p(f) \)

Simulation parameters:

\[ \omega \rightarrow (f) = \omega \leftarrow (f) = \omega_0 e^{-\Delta E_0 (1 - f/f_0)^{3/2}} \]

\[ \Delta E_0 = 10 k_B T, \quad \omega_0 = 1 \text{ MHz}, \quad a = 0.25 \text{ nm}, \quad f_0 = 3 \text{ nN} \]

Solution of the rate equation

\[ \kappa v p'(f) = -\left(\omega^+ (f) + \omega^- (f)\right) p(f) + \omega^+ (f + \kappa a) p(f + \kappa a) + \omega^- (f - \kappa a) p(f - \kappa a) \]

\[ \sum_n p(f + n \kappa a) = 1 \]

- **Solution Ansatz:**
  \[ p(f) = P(f) - P(f - \kappa a), \quad P(f) = \sum_{n=0}^{\infty} p(f - n \kappa a) \]
  \[ P(\infty) = 1, \quad P(-\infty) = 0 \]

- **Approximations:**

  - **Large** \( \kappa a \): \[ P(f) \approx \frac{1}{\kappa v} \int_{-\infty}^{f} df' \left( \frac{1}{f} \int_{f'}^{f} df'' \left( \omega^+ (f'' + \kappa a) + \omega^- (f'') \right) \right) \]

  - **Small** \( \kappa a \): \[ P(f) \approx \frac{1}{2} \operatorname{erf} \frac{f - \bar{f} + \kappa a / 2}{\sigma} \]

  where \( \nu = a \omega^+ (\bar{f}) \frac{\sinh x}{x} e^{\frac{x}{2 \left( 1 - L(x) \right)}} \left( 1 - e^{-4 \frac{\bar{f} x}{\kappa a}} \right) \), \( x = \frac{\kappa a}{2} \frac{d \ln \omega^+ (\bar{f})}{df} \)

  \[ \sigma^2 = \frac{(\kappa a)^2}{2x} \left( 1 - L(x) \right) \]; \( L(x) = \coth x - x^{-1} \)

\[ \omega^\rightarrow (f) = \omega_0 \exp\left(-\frac{\Delta E_0 (1 - f / f_0)^{3/2}}{k_B T}\right) \]

\[ \omega_0 = 1 \text{ MHz}, \quad \Delta E_0 = 10 k_B T \]

\[ a = 0.25 \text{ nm}, \quad f_0 = 3 \text{ nN} \]

\(\kappa = 0.1 \text{ N/m} \) (black), 0.5 N/m (red), 3 N/m (green), 5 N/m (blue)

Slip statistics

- Rate equation for the no-jump probability
  \[ \frac{d\pi(t)}{dt} = -\omega(f(t))\pi(t) ; \quad f(t) = \kappa vt \quad \Rightarrow \quad \kappa v \frac{d\pi(f)}{dt} = -\omega(f)\pi(f) \]

- Transition rate follows immediately:
  \[ \omega(f) = -\kappa v \frac{d\pi(f)}{df} = -\kappa v \frac{d\ln\pi(f)}{df} \]

- Experimentally:
  \[ \pi_v^{\exp}(f) = \frac{\text{# of jumps after force value } f}{\text{total # of jumps}} \]

- Better to work with
  \[ g_v(f) = -\kappa v \ln\pi_v(f) = \int_0^f df' \omega(f') \]

- Validity test of the rate equation: \( g_v(f) \) should be independent of pulling velocity

Experimental results

- Experimental details:
  - HOPG
  - Pressure = $2 \times 10^{-10}$ mbar
  - Transitions in between hexagon centers

- Collapse of the experimental $g$-functions onto a single master curve for $v > 90$ nm/s

- No collapse for slower pulling speeds indicates contact aging

- Aging time: $t_{\text{aging}} \sim (0.25 \text{ nm})/(90 \text{ nm/s}) \sim 3 \text{ ms}$

Contact aging

• The model:

• Rates:

\[
\omega_{A,B}(f) = \Gamma_{A,B} \exp \left[ - \frac{\Delta E_{A,B}}{k_B T} \left( 1 - \frac{f}{F_{A,B}} \right)^{\alpha_{A,B}} \right]
\]

\[
\Omega = \Omega_0 e^{-\Delta E/k_B T}
\]

• Additional assumptions:

\[ \alpha_A = \alpha_B ; \quad \frac{F_A}{F_B} = \frac{\Gamma_A}{\Gamma_B} = \frac{\Delta E_A}{\Delta E_B} \]

• Fit values:

\[ \Delta E_A = 24 k_B T ; \quad F_A = 0.19 \text{nN} ; \quad \alpha_A = 2.4 ; \quad \Gamma_A = 12 \text{ms}^{-1} \]

\[ \Delta E_B = 32 k_B T ; \quad \Omega = 10 \text{s}^{-1} \]

M.E., A. Schirmeisen, L. Jansen, H. Fuchs, and P. Reimann,
Nonmonotonic $T$- and $v$-dependent friction

- The model:
  \[
  \omega_{A,B}(f) = \Gamma_{A,B} \exp \left[ -\frac{\Delta E_{A,B}}{k_B T} \left( 1 - \frac{f}{F_{A,B}} \right)^{\alpha_{A,B}} \right] 
  \]

\[
\Omega = \Omega_0 e^{-\Delta E / k_B T}
\]

- Rates:

\[
\omega_{A,B}(f) = \Gamma_{A,B} \exp \left[ -\frac{\Delta E_{A,B}}{k_B T} \left( 1 - \frac{f}{F_{A,B}} \right)^{\alpha_{A,B}} \right] 
\]

- Slow pulling or high temperature
  \[\Omega > v / a\]
  state B

- Fast pulling or low temperature
  \[\Omega < v / a\]
  state A

- Intermediate pulling speed or intermediate temperature
  \[\Omega \approx v / a\]
  anomalous friction behavior:
  \[\partial \langle f \rangle / \partial v < 0 ; \quad \partial \langle f \rangle / \partial T > 0\]
Nonmonotonic $T$- and $v$-dependent friction

- The model:

$\omega_{A,B}(f) = \Gamma_{A,B} \exp \left[ -\frac{\Delta E_{A,B}}{k_B T} \left( 1 - \frac{f}{F_{A,B}} \right)^{\alpha_{A,B}} \right]$ \hspace{1cm} \Omega = \Omega_0 e^{-\Delta E / k_B T}$

- Rates:

- Symbols: experiment
  (a): HOPG
  (b): NaCl
  Barel et al, PRB 84, 115417 (2011)

- Lines: simulations
  M.E. and P.Reimann, PRX 3, 041020 (2013)
Conclusions

- Interstitial jumps of the AFM cantilever tip are thermally activated events, resulting in a logarithmic force-velocity relation.

- Analytical results for the force probability distribution are obtained within the rate theory.

- The data analysis method is introduced, which allows one to check the validity of the rate equation and deduce the transition rates.

- Experimental application of this method to the real system indicated that the rate equation holds only at high pulling speeds.

- Discrepancy at slow pulling is explained as resulting from contact aging.

- A simple contact aging model explains the statistics of the slip events and a non-monotonic temperature and velocity dependence of friction.