Velocity dependence of adhesion in a sliding nanometer-sized contact

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Motivations

• Capillary adhesion is involved in a high number of natural and industrial phenomena (granular media, friction in devices...)


• Little is known about the evolution of the capillary forces in a sliding contact

No direct experimental investigation

• What about existing models?
Capillary adhesion

- Water condensation on hydrophilic surfaces

\[ R_2 \approx R_K \approx 1 - 2 \, nm \]

\[ \frac{1}{R_K} \approx \left[ \frac{k_B T}{\gamma_{LV} v_M} \right] \ln \left( \frac{P}{P_S} \right) \]

The volume of the capillary meniscus is dependent on the static contact angle with water of the surfaces in contact, on the relative humidity and on the tip radius.

Capillary adhesion

- The Laplace pressure in the meniscus generates an adhesive force \( F_{\text{capillary}} = \Delta P \times \text{WetContactArea} \)

- For AFM experiments and hydrophilic surfaces,
  \[
  F_{\text{capillary}} = 2\pi R_{\text{probe}} \gamma_{\text{LV}} \times (\cos \theta_{\text{sample}} + \cos \theta_{\text{probe}}) = 10\text{-}100 \text{ nN}
  \]
  \( \theta \): Meniscus static contact angle with water

- Capillary forces are comparable to the acting normal load in friction at the nanoscale

- Capillary force adds to the external applied load \( (F_N) \) and plays an indirect role in friction mechanisms.
  \[
  F_F = \mu (F_{\text{adhesion\sim capillary}} + F_N)
  \]
Capillary adhesion in a sliding contact

- Multi-asperity contact
- Meniscus nucleation needs time (1 ms)
- Thus, capillary force is sliding velocity dependent
- The linear decrease of the friction force is related to the vanishing of the capillary forces

Riedo et al. PRL 88 (2002) 185505
AFM experimental limitations

• AFM back and forth scanning:
  Meniscus *nucleates and grows* during stop periods but *vanishes* during sliding

• Is that possible to achieve a stationary state?

• Is that possible to measure directly the capillary adhesion force as a function of the sliding velocity?
AFM experimental limitations

**AFM circular mode**

- Probe is submitted to a circular displacement in the plane of the surface:
  - Circular frequency: 100 Hz
  - Circular radii: 0 nm to 1500 nm
  - Sliding velocities: 0 to 1 mm.s\(^{-1}\)
- Relative displacement at constant and continuous velocity: **Stationary state**
- Combination of the circular mode with the force spectrum mode:
  - Measurement of adhesion forces as a function of the sliding velocity

Circular tracks on a GaAs sample obtained with the circular mode
**Experimental set-up**

**Principle**

- **Si$_3$N$_4$** probes $R = 15-40$ nm, $\theta = 70^\circ$
- Retracting velocity is set at a constant value of $0.1\mu$m.s

### Hydrophobic Surfaces

<table>
<thead>
<tr>
<th></th>
<th>$R_q$ (nm)</th>
<th>$\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPG</td>
<td>0.05</td>
<td>105</td>
</tr>
<tr>
<td>Si$_{CH3}$</td>
<td>0.20</td>
<td>100</td>
</tr>
</tbody>
</table>

### Hydrophilic Surfaces

<table>
<thead>
<tr>
<th></th>
<th>$R_q$ (nm)</th>
<th>$\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mica</td>
<td>0.03</td>
<td>5</td>
</tr>
<tr>
<td>Si</td>
<td>0.16</td>
<td>60</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>0.34</td>
<td>70</td>
</tr>
<tr>
<td>Gold</td>
<td>0.23</td>
<td>75</td>
</tr>
</tbody>
</table>
Hydrophilic surface – Gold CVD

![Graph showing force vs. Z Piezo displacement for two different speeds: a) V = 6 μm.s⁻¹ and b) V = 600 μm.s⁻¹.](image)
Hydrophilic-hydrophobic surfaces
Adhesion vs Sliding velocity

3 Regimes:
1: Meniscus at the equilibrium state
2: Meniscus not at the equilibrium state
3: No more capillary meniscus

$V_{start}$ defines a threshold sliding velocity from which the capillary meniscus cannot reach its equilibrium state anymore.
In regime 2, the adhesive force decreases linearly with a logarithmic increase of the sliding velocity. This suggests a thermally activated process, like a growth process of a capillary meniscus, in which water molecules have to overcome energy barriers due to surface defects.
Model based on
the growth process of a capillary meniscus

The sliding velocity, $V$, is related to the time, $t$, needed to overcome the total distribution of energy barriers due to surface defects

$$t = t_0 \cdot \exp\left[\frac{\Delta E}{k_B T}\right]$$

Then

$$V \propto t^{-1} \propto \exp\left[-\frac{\Delta E}{k_B T}\right]$$

In a first approximation, $\Delta E$ is proportional to the perimeter of the wet contact areas

$$\Delta E \propto \sqrt{R_{\text{probe}} R_K} \sqrt{\cos \theta_{\text{probe}} + \cos \theta_{\text{sample}}}$$

and at $V = V_{\text{start}}$

$$\ln(V_{\text{start}}) \propto \sqrt{R_{\text{probe}} R_K} \sqrt{\cos \theta_{\text{probe}} + \cos \theta_{\text{sample}}}$$
Experimental dependence of $\ln(V_{\text{start}})$ on contact angle

$$\ln(V_{\text{start}}) \propto \sqrt{R_{\text{probe}} R_K} \sqrt{\cos \theta_{\text{probe}}} + \cos \theta_{\text{sample}}$$

Experimental conditions:
- Different surfaces
- Humidity 40%
- Same probe ($R_{\text{probe}} = 30 \text{ nm}$)
- $R_{\text{probe}} R_K = \text{Constant}$
- Temperature = constant

![Graph](image_url)
Conclusions

- Innovative experimental set-up: AFM circular mode
- Direct experimental evidence of a linear decrease of the capillary forces with a logarithmic increase of the sliding velocity, for hydrophilic surfaces.
- This dependence could be related to a thermally activated growth process of the capillary meniscus.
- The energy barrier is linked to the meniscus perimeter (humidity, probe radius and contact angles)
Acknowledgements / References of our work

• Agence Nationale de la Recherche: Pénélope par Médée - ANR 08 JCJC 0051 01
• Elisabeth Charlaix and Denis Mazuyer

• Int. Patent PCT/FR2011/05102