Contact and friction of thin hydogels films: the role of poroelasticity

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Motivations

Functionalization of glass substrates by hydrophilic coatings

Ex: prevention of mist formation

→ Tribological performance: friction, scratch resistance?

Thin hydrogels layers mechanically confined within contacts between rigid substrates

- Stress amplification as compared to bulk hydrogel substrates
- Enhanced drainage of the highly swollen gel network

Role of poroelasticity on mechanical and frictional properties?
Model gel networks

• **Poly(PEGMA)**

\[
\text{H}_3\text{C}\left[\text{O-}\right]_n\text{O-}\text{CO-CH}_2\text{CH}_3
\]

poly(ethylene glycol) methyl ether methacrylate
PEGMA (n = 4/5)

• **Poly(DMA)**

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{C}=\text{N}\text{O}
\]

N,N-dimethylacrylamide

Rubbery

\[\Phi_g \approx 0,18 \text{ vol/vol}\]

Glassy

**Tiol-ene chemistry route → homogeneous thin films:**

- grafted to glass or silicon wafer substrates
- controlled thickness from 250 nm (± 5%) to 2 µm (± 10%)
- controlled cross-linking (swelling ratio from 2.5 to 4)

*Li et al, Langmuir, 2015
Chollet et al, ACS Appl. Mat. Interfaces, 2016*
Normal indentation response

Time-dependent indentation depth

Poly(PEGMA) $e_0=9$ µm  $R=5.2$ mm
Approximate poroelastic contact model

Within the limits of confined contact geometries \( a \gg e_0 \)

- No expansion of film deformation outside the contact
- Compression of the layer within the contact without lateral expansion
  \( \rightarrow \) only vertical displacement components are accounted for
- Rigid substrates

Compressive strain

\[
e(\tau, t) = \frac{c_0 - c(t)}{c_0} = \frac{\delta(t) - r^2/2R}{c_0}
\]
**Indentation kinetics**

Mixture theory developed by Biot (1955)

- Normal contact stress:  \( \sigma(r, t) = \tilde{E} \varepsilon(r, t) + p \)

Elasticity of the polymer network

\[
\tilde{E} = \frac{2G(1-\nu)}{1-2\nu} \quad \text{Uniaxial compression modulus}
\]

Pore pressure

- Water transport driven by Darcy’s law:  \( J_r = -\kappa \frac{dp}{dr} \)

\( \kappa = \frac{D_p}{\eta} \)

- Volume conservation

\[
\frac{t}{\tau} = -\frac{\delta}{\delta_\infty} + \frac{1}{2} \log \left( \frac{1 + \delta/\delta_\infty}{1 - \delta/\delta_\infty} \right)
\]

\( \delta_\infty = \left[ \frac{F_n e_0}{\pi R \tilde{E}} \right]^{1/2} \)

Equilibrium indentation depth

\( \tau = \frac{1}{2\sqrt{\pi}} \frac{\eta}{D_p} \left( \frac{F e_0 R}{\tilde{E}^3} \right)^{1/2} \)

Poroelastic time
Fit of experimental data to the poroelastic contact model

\[ \Delta = \frac{\delta}{\delta_\infty} \]

\[ T = \frac{t}{\tau} \]

Poly(PEGMA) \( e_0 = 9 \, \mu m \)

- \( R = 20.7 \, mm \), \( F = 7 \, mN \), \( F = 88 \, mN \)
- \( R = 5.2 \, mm \), \( F = 32 \, mN \), \( F = 11.5 \, mN \)
Characteristic poroelastic time $\tau$

$\tau \propto (F_n e_0 R)^{1/2}$

$5 < e_0 < 9 \mu m$

$5.2 < R < 20.7 \text{ mm}$
Equilibrium indentation depth

Poly (PEGMA)

\[ \delta_{\text{dry}} = 9 \, \mu m \]

\[ \delta_{\text{dry}} = 5 \, \mu m \]

\[ R = 5.2 \, \text{mm} \, \text{and} \, 20.7 \, \text{mm} \]

\[ 0.42 \times \]

\[ \delta_{\infty} \propto \left( \frac{F_n e_0}{R} \right)^{1/2} \]

Poly (DMA)

\[ \delta_{\text{dry}} = 4.5 \, \mu m \]

\[ \phi_g \]

\[ R = 5.2 \, \text{mm} \, \text{and} \, 20.7 \, \text{mm} \]

Deviation from the model

Close to \( \phi_g \)
Glass transition induced by poroelastic drainage

- Lateral contact experiments $\rightarrow$ shear modulus measurements during the course of indentation drainage

\[
\Delta = \Delta_0 \sin(\omega t) \quad \Delta_0 \leq \pm 100 \text{nm}
\]

**Poly(PDMA)**

Storage shear modulus $G'$ (Pa)

Increasing $F_n$

**Poly(PEGMA)**

Storage shear modulus $G'$ (Pa)

Increasing $F_n$

$F_n$ from 4.5 to 13.7 N

No transition

Glass transition
Steady-state friction: \text{poly(DMA)} \text{ with } \phi > \phi_g

\textbf{Friction force}

- \text{Velocity-dependence: two regimes} \rightarrow \text{poroelastic effect?}

\begin{itemize}
  \item $F_n = 600 \text{ mN}$
  \item $F_n = 200 \text{ mN}$
  \item $F_n = 50 \text{ mN}$
  \item $e_0 = 3.1 \mu m$
\end{itemize}

\textbf{Contact shape}

- [Images of contact shapes at different loads]
Contribution of poroelasticity : Peclet number

\[ Pe = \frac{2a}{v\tau} \]

\[ \frac{\text{Contact time}}{\text{Poroelastic time}} \]

Contact radius

Friction force

\( Pe > 1 \) : drainage equilibrium \( \sim \) normal indentation

\( Pe < 1 \) : out-of equilibrium state \( \rightarrow \) incomplete drainage

\( \tau \) determined independently from indentation experiments
Pore pressure distribution

- Extension of the poroelastic contact model to steady-state sliding

Moving coordinate system

\[ \frac{\partial}{\partial t} \bigg|_{x,y} \rightarrow -v \frac{\partial}{\partial x} \]

Pore pressure field induced during lateral motion

\[ -v \frac{\partial \epsilon}{\partial x} = -\kappa \nabla^2 p \]

Darcy’s Law

General solution for pore pressure:

\[ p = -\frac{v}{8 R e_0 \kappa} r^3 \cos \theta + \sum_{n=0}^{\infty} a_n r^n \cos n\theta \]

With \( p=0 \) on the contact line to be determined
Contact stress: velocity dependence

Hyp: we enforce that contact line is a circle with $p(a_0)=0$

$$\sigma(r, t) = \tilde{E} c(r, t) + p$$

$$\sigma(r, \theta) = \frac{\tilde{E}}{2Re_0} \left( a_0^2 - r^2 \right) \left[ 1 + \frac{v}{4\tilde{E}\kappa} r \cos \theta \right]$$

**Critical velocity $v_c$**

$$v_c = \frac{4\tilde{E}\kappa}{a_0}$$

$Pe = 1$

Above $v_c$: negative contact stress $\rightarrow$ contact line shrinks non-uniformly
Reduction in contact size $\rightarrow$ build-up of pore pressure at increasing velocities
Contact size reduction for $\text{Pe} < 1$

- Numerical solution of the poroelastic contact model

Contact line $a(\theta,v)$ ensuring:

$$\sigma(r, \theta) > 0$$

$$p(r = a(\theta,v)) = 0$$

$$\int_{A} \sigma(r, \theta) = F_n$$

Calculated contact shape and normal contact stress

$$\text{Pe}=0.1$$
Conclusions & perspectives

- Indentation of thin hydrogels films confined within glass substrates
  - Approximate poroelastic contact model
    - Scaling laws for $\delta_\infty$ and $\tau$ as a function of - gel mechanical and diffusive properties
      - contact geometry & loading conditions
  - Glass transition induced by drainage

- Frictional properties driven by poroelastic time
  - Two frictional regimes - $Pe > 1$ equilibrium drainage state
    - $Pe < 1$ pressure imbalance resulting in contact asymmetry and size reduction

→ Contact changes accounted for by poroelasticity

Contribution to friction force of viscous dissipation associated to poroelastic flow?

Friction force across glass transition?