Supplemental Materials: The role of crosslinking density in surface stress and surface energy of soft solids

Weiwei Zhao,[1] Jianhui Zhou,[1] Haitao Hu,[1] Chang Xu,[2] and Qin Xu[1, 3, *]

[1] *Department of Physics, The Hong Kong University of Science and Technology, Hong Kong, China*
[2] *School of Physical Science, University of Science and Technology of China, Hefei, China*
[3] *HKUST Shenzhen Research Institute, Shenzhen, China*

I.   MEASUREMENTS OF THE SURFACE STRESSES OF LIQUID DROPLETS

We measured the surface stress of Newtonian liquids (including glycerol, fluorinated oil and silicone oil) by numerically analyzing their droplet profiles. The images of both sessile and pendant droplets were taken by a digital Nikon D5600 camera equipped with a 105 mm macro-lens. The droplet edges were resolved by using the Canny boundary detector. The surface curvatures at the droplet interface (κ) result from the balance between the Laplace pressure and the hydrostatic pressure,

$$2\Upsilon_l(\kappa - \kappa_0) = \pm\Delta\rho g z \tag{1}$$

where κ_0 is the curvature at the apex and $\Delta\rho$ is the density difference between the droplet and the surrounding medium. Since we only measured droplets in air, the density difference $\Delta\rho$ can be replaced by liquid density ρ. The sign, " $\pm$ " , on the right-handed side of Eq. 1 is determined by whether the image was taken for a sessile droplet ($+$) or a pendant droplet ($-$). Notice that the droplet profiles were measured in equilibrium states. In soft wetting experiments, we systematically compared the advancing and receding contact angles of liquids wetting on the soft gels. When the crosslinking density varied from $k = 0.91\%$ to 1.33%, we observed no contact angle hysteresis.

Considering the axial symmetry of the droplet profiles, the boundary can be projected onto a 2D rz-coordinate plane (see Fig.S1 a). We use s and ϕ to denote the arc length and the angle of the slope at the boundary interface, respectively. Therefore, $dx = ds\cos\phi$ and $dz = ds\sin\phi$. Therefore, Eq. 1 can be rewritten in a parametric form,

$$\begin{cases} \mathrm{d}X = cos\phi\ \mathrm{d}S \\ \mathrm{d}Z = sin\phi\ \mathrm{d}S \\ \mathrm{d}\phi = (2 - sin\phi/X \mp \beta_0 Z)\mathrm{d}S, \\ \beta_0 = \Delta\rho g R_0^2/\Upsilon_l \end{cases} \tag{2}$$

where the coordinates (x, z, s) are normalized to the dimensionless variables $X = x/R_0, Y = y/R_0$ and $S = s/R_0$. We can calculate the droplet profile numerically through the iterations of Eq. 2. The droplet surface stress Υ_l is considered to be successfully determined when the numerical result fits well with the imaged droplet profile. Equations 1 and 2 can be applied to both pendant (Fig. S1b) and sessile droplets (Fig. S1c).

II.   CONFOCAL MICROSCOPY IMAGING OF THE LOCAL WETTING PROFILES

To place the tracers on the surfaces of soft silicone gels, we deposited a solution droplet containing 200-nm beads on the surfaces of the cured gels for at least 3 h. During the coating process, the entire sample was sealed properly to avoid any evaporation. A fraction of the beads in the solution diffused to the gel and adhered to the interface. As a result, a layer of nicely coated fluorescent beads was left on the gel surfaces when the solution was removed. In the soft wetting experiments, we used a spinning-disk laser confocal microscope (Lecia SP8) to image the region close to the contact point. By locating the fluorescent beads in 3D, we can reconstruct the wetting profiles by using our previously developed MATLAB codes (as shown in Fig. S2 a-d). Due to axial symmetry of the droplet geometry, all of the wetting profiles are collapsed to the 2D $r - z$ plane. For each gel substrate, we varied the droplet radius and collapsed the wetting profiles near the contact point to confirm the validity of the Neumann's triangle (Fig. S2 e).

---

* qinxu@ust.hk

III. WETTING PROFILES ON THE GELS WITH REDUCED FREE CHAINS

To investigate the role of free chains in surface stress measurements, we performed control experiments on gel surfaces with reduced amounts of uncrosslinked polymers. The samples were prepared through the following three steps. First, a cured gel substrate coated on a glass slide was submerged in a 50% toluene solution mixed with 50% ethanol for 24 h. The process greatly swelled the gel networks and extracted uncrosslinked polymers by osmotic pressure near the gel interfaces. Second, we removed the surrounding solution containing the free chains and then waited for another 24 h for the toluene and ethanol to dry out. Third, we repeated the first two steps again to further reduce the amount of free chains near the interfaces. This treatment decreased the substrate mass by approximately 15% without generating creasing instabilities on the gel surfaces. Figures S3 a and b show the wetting profiles before and after the treatment for $k = 1.3\%$ and $k = 1.1\%$, respectively.

IV. A CONTINUUM ELASTIC MODEL FOR SOFT WETTING

In this work, we extended the linear elastic theory proposed by Style, et al. (Ref.[29] in the paper) to soft wetting with a given contact angle θ. The calculation assumes that $\Upsilon_{gl} \approx \Upsilon_{ga} = \Upsilon_g$, which is consistent with the experiments on glycerol droplets. The governing equations of the displacement and stress fields, $(\mathbf{u}(r,z))$ and $(\overleftrightarrow{\sigma}(r,z))$, of the substrate are

$$(1 - 2\nu)\nabla^2\mathbf{u} + \nabla(\nabla \cdot \mathbf{u}) = 0, \tag{3}$$

$$\overleftrightarrow{\sigma} = \frac{2}{1+\nu}[\frac{1}{2}((\nabla\mathbf{u})^T + \nabla\mathbf{u}) + \frac{\nu}{1-2\nu}(\nabla \cdot \mathbf{u})\mathbf{I}]. \tag{4}$$

Considering the boundary conditions due to the gel surface stress and liquid surface tension

$$\sigma_\Upsilon = \Upsilon_g\frac{1}{r}\frac{\partial}{\partial r}(r\frac{\partial u_z}{\partial r})\hat{z}, \tag{5}$$

$$t(r, z = h) = \gamma_l \sin\theta\delta(r - R\sin\theta)\hat{z} - \frac{2\gamma_l}{R}H(R\sin\theta - r)\hat{z} - \gamma_l \cos\theta\delta(r - R\sin\theta)\hat{r}, \tag{6}$$

we can solve equations by applying Hankel transformations to both the displacement $u_z(r,z)$ and stress fields $\sigma(r,z)$. As a result, the surface profile $u_z(r, z = h)$ can be written as

$$\begin{aligned}
u_z(r,h) = \int_0^{+\infty} & ds\ \gamma_l s J_0(sr) \\
& (J_1(sR\sin\theta)s(\nu+1)\cos\theta\left(2h^2s^2 + (2(5 - 4\nu)\nu - 3)\cosh(2hs) + 2\nu(4\nu - 5) + 3\right) \\
& + 2J_0(sR\sin\theta)Rs\left(\nu^2 - 1\right)\sin\theta((4\nu - 3)\sinh(2hs) + 2hs) \\
& - 4J_1(sR\sin\theta)\left(\nu^2 - 1\right)((4\nu - 3)\sinh(2hs) + 2hs)) \\
& /(s^2(E\left(2h^2s^2 + 4\nu(2\nu - 3) + 5\right) + E(3 - 4\nu)\cosh(2hs) \\
& + 4\Upsilon_g hs^2\left(\nu^2 - 1\right) + 2\Upsilon_g s(\nu - 1)(\nu + 1)(4\nu - 3)\sinh(2hs))).
\end{aligned} \tag{7}$$

The dashed lines in the Fig. 2a of the main manuscript were calculated by using Eq. 7 with the experimental parameters for various cross-linking densities. The Poisson ratio was chosen as $\nu = 0.46$ in the calculations, which is consistent with the results obtained from our previous measurements (see Ref. [22] in the main manuscript).
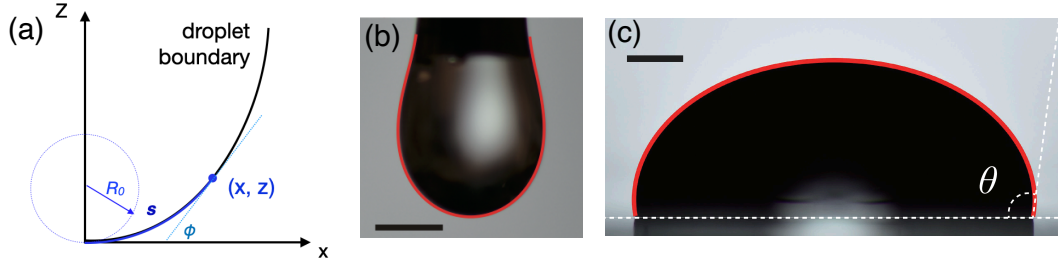
FIG. S1. **a**. A schematic illustration of the droplet profiles defined by the parametric coordinates (s, ϕ). **b**. A pendent droplet with the fitted droplet boundary (the red solid line). Scale bar: 1mm. **d**. A sessile droplet with the fitted droplet boundary (the red solid line). Scale bar: 500 μm.
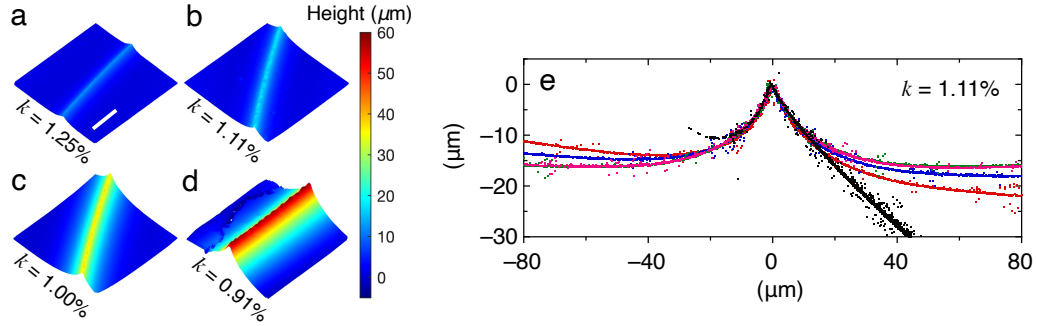

FIG. S2. **a - d**. Reconstructed three-dimensional surface profiles from confocal microscope measurements of the gel substrates for $k = 1.25\%, 1.11\%, 1.0\%$, and $0.91'\%$, respectively. The color bar indicates deformations along z. The scale bar in the x-y plane indicates 50 μm. **e**. The collapsed wetting profiles induced by different sizes of droplets for $k = 1.11\%$.
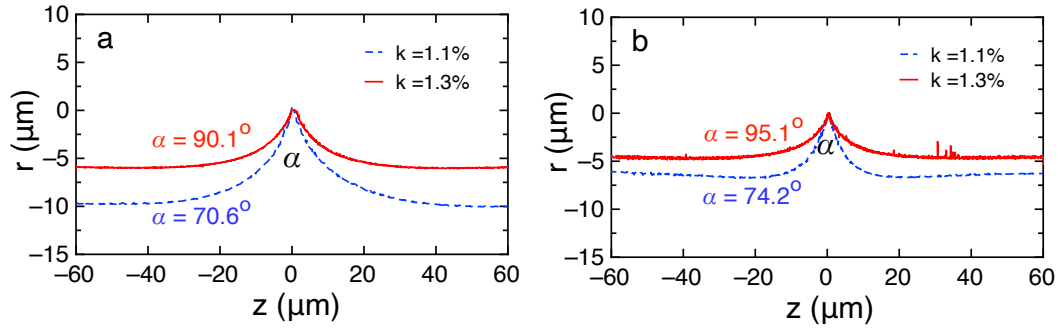

FIG. S3. The wetting profiles before (a) and after (b) the swelling and drying procedures for two different crosslinking densities $k = 1.1\%$ (blue dashed line) and $k = 1.3\%$ (red solid line), respectively. In both panels (a) and (b), we observed the same trend that the opening angle α increases with the crosslinking density k.