Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

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Supplementary Note

Estimation of contact line force at tip-liquid contact interface

Contact line force F_{line} is given by the sum of the tangential components of the surface tension around the three phase contact line at tip-liquid contact interface. For the liquid bridge in equilibrium, the tip-liquid contact angle φ (Fig. 3a in the main text) exhibits constant value around the contact line, and F_{line} becomes zero in lateral direction. However, when the tip moves, hydrodynamic viscous damping near the contact line can induce a change in the angle φ [S1], and thus F_{line} can have a finite value in magnitude.

Specifically, when $x=\pm A$, the tip velocity is zero, so is the fluid velocity near the contact line. Thus, hydrodynamic viscous force occurring near the contact line and the resultant contact line force are zero at $x=\pm A$, i.e., $F_{\mathrm{line}}=0$ at $x=\pm A$. However, when $x=0$, the tip shears the fluid with velocity $v=wA$, which bends the liquid-air interface and changes the contact angle. The angle change at $x=0$ is estimated as $\varphi^3-\varphi_{\mathrm{eq}}^3=9\ Ca\ l$ [S1], where Ca is the capillary number and $l=\log(l_{\mathrm{m}}/l_0)$ is the ratio of macroscopic to microscopic length scales. The logarithmic factor l typically falls into the range of 1~100, and Ca is given by $\mu wA/\gamma$, where μ is the viscosity of liquid, γ the surface tension, w the angular frequency, and A the tip oscillation amplitude. Notice that the photo images (Fig. 2a in the main text) show $\varphi_{\mathrm{eq}}=\pi/2$, and the angle change $\Delta\varphi$ should be negligible, $\Delta\varphi\ll 1$, because the micro-sized nanoliter volume liquid bridge is sheared only by nanoscale amplitude (about 1 nm). This leads to $\Delta\varphi/A=\mu wl/(3\gamma\ \varphi_{\mathrm{eq}}^2)\approx 3.28\times10^{-5}$ rad/nm even for $l=100$. Such an angle change generates a net force F_{line} at $x=0$, which is non-negligible, and leads to the hysteresis in the force-distance curve, as schematically described in Fig. 3c (middle) in the main text. The energy dissipation, proportional to the enclosed area of the force hysteresis curve, is measured by the damping $b_{\mathrm{int}}w$ $(=E_{\mathrm{dis}}/(\pi A^2))$ in dynamic force spectroscopy, and is approximately given by $b_{\mathrm{int}}w\approx\pi R_{\psi}\gamma(\Delta\varphi/A)\sin\varphi_{\mathrm{eq}}$, where R_{ψ} is the tip radius (see Supplementary Equation 3 in Ref [S2]). For the tip we used ($R_{\psi}=125/2\ \mu$m), the contact line-induced damping is estimated by 0.5 N/m, which is reasonably comparable to the experimental results (see the text for details).

References

[S1] Cox, R. G. The dynamics of the spreading of liquids on a solid surface. *J. Fluid Mech.* **168**, 169–194 (1986).

[S2] Lee, M., Kim, B., Kim, J. & Jhe, W. Noncontact friction via capillary shear interaction at nanoscale. *Nat. Commun.* **6**, 7359 (2015).

Derivation of contact area force at tip-liquid contact interface

A shear harmonic oscillator interacting with a confined fluid (Fig. 3b in the text) is described as

$$\mathrm{m}\ddot{x} + b\dot{x} + kx = Fe^{iwt} + F_{\mathrm{area}}\,, \tag{1}$$

where m is the effective mass of the probe, b the intrinsic damping constant, k the stiffness of the probe, Fe^{iwt} the driving force, and F_{area} the liquid-mediated shear force exerted on the contact area. While the contact area force F_{area} is given by the tensor product of the contact area σ and the stress tensor τ_{ij} at the contact interface, we only consider xz-component of stress tensor τ_{ij} due to the present two-dimensional symmetry of the system to obtain F_{area} such as

$$F_{\mathrm{area}} = \sigma\,\tau_{xz}(h,t) = -\sigma\,\eta \frac{\partial U}{\partial z}\Big|_{z=h}, \tag{2}$$

where $U(z,t)$ is the velocity filed of the fluid in the x-direction and governed by Navier-Stokes equation. For incompressible Newtonian fluid with the two-dimensional symmetry, the Navier-Stokes equation for $U(z,t)$ is reduced to

$$\frac{\partial U}{\partial t} = \frac{\eta}{\rho}\frac{\partial^2 U}{\partial z^2}\,, \tag{3}$$

with no-slip boundary conditions at the upper and lower interfaces,

$$U(z = h, t) = \dot{x}(h,t), \tag{4}$$

$$U(z = 0, t) = 0. \tag{5}$$

Since the entire system is oscillatory driven, we assume periodic solutions for the probe motion $x(h,t)$ and fluid velocity $U(z,t)$ in the forms

$$x(h,t) = A(h)\ \mathrm{Exp}\left[i\left(wt + \theta - \frac{\pi}{2}\right)\right], \tag{6}$$

$$U(z,t) = u(z)\ \mathrm{Exp}[(wt + \theta)]. \tag{7}$$

By inserting Eqs. (6,7) into Eqs. (1-3) and applying the two boundary conditions Eqs. (6,7), we obtain the solutions $x(h,t)$ and $U(z,t)$ as well as $F_{\mathrm{area}}(h, t)$ (Eq. (2)). Here, the oscillatory force $F_{\mathrm{area}}(h, t)$ can be represented by a force proportional to the probe oscillation $x(h,t)$ as

$$F_{\mathrm{area}} = -\kappa\,(1 + \mathrm{i})\cot\left[\frac{(1-\mathrm{i})h}{\delta}\right] x(h,t), \tag{8}$$

where $\delta=(2\eta/(w\rho))^{1/2}$ and $\kappa=\sigma\, w^{3/2}\,(\eta\rho/2)^{1/2}$. We note that the penetration depth δ is about 4 μm in the current system, whereas the tip height $h \approx 100$ μm. Thus, using the relation, $\cot[(1-i)a] \rightarrow i$ as $a \rightarrow \infty$, equation (8) is simplified to $F_{\mathrm{area}} = -\kappa(-1+i)\,x(h,t)$. Further, since $\dot{x}(h,t) = iw\,x(h,t)$ for the oscillatory solution (Eq. (6)), we can decompose F_{area} into the position-dependent and the velocity dependent forces,

$$F_{\mathrm{area}} = \kappa\,x(h,t) - (\kappa/w)\,\dot{x}(h,t). \tag{9}$$

By comparing Eq. (9) with $F_{\mathrm{area}} = -k_{\mathrm{int}}\,x - b_{\mathrm{int}}\,\dot{x}$, we get the elastic and damping coefficients of the interaction as follows,

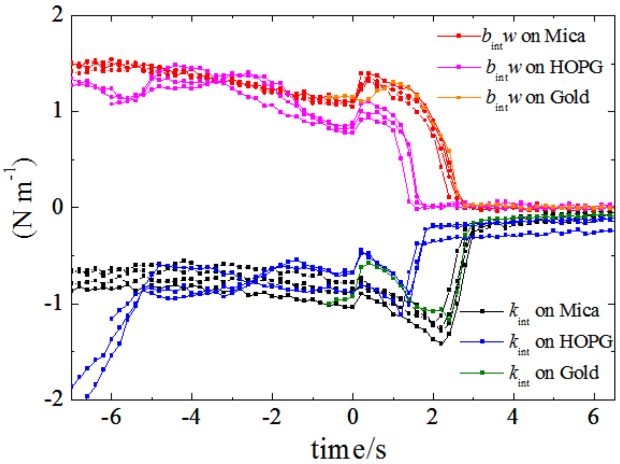
$$k_{\mathrm{int}} = -b_{\mathrm{int}}w = -\kappa = -\sigma\,\mathrm{w}^{3/2}\sqrt{\eta\rho/2}. \tag{10}$$

Therefore, the contact area interaction results in the negative-valued elasticity k_{int} and positive damping $b_{\mathrm{int}}w$, as observed in the experiments (Fig. 2c in the text). Equation (10) relates the elastic coefficient k_{int} of the interaction with the fluid viscosity η, from which we finally obtain

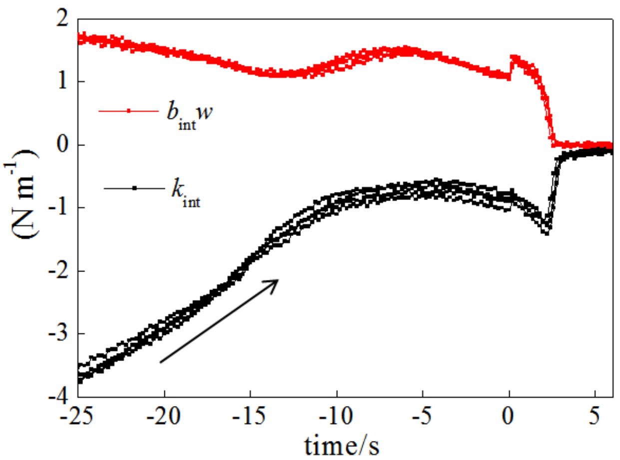
$$\eta = 2(k_{\text{int}})^2/(\sigma^2 w^3 \rho). \quad (11)$$

We experimentally measure k_{int} by DFS method, and derive the viscosity η using Eq. (11).

Supplementary Figure



Supplementary Figure 1. Independency of substrates used. The measured negative elasticity k_{int} and positive damping $b_{\text{int}}w$ show almost identical behaviors for various types of substrates used, which demonstrates that our AFM-based platform for determination of viscosity is not sensitive to the specifics of substrates.



Supplementary Figure 2. Decrease of $|k_{\text{int}}|$ with evaporation. The negative elasticity k_{int} in the nanoliter-volume water bridge varies more significantly, compared to the damping $b_{\text{int}}w$, during the dynamic force measurements. In particular, the magnitude of the elasticity decreases as the volume of the sheared bridge decreases due to evaporation (black arrow), which indicates that the measured elasticity is associated with the total mass of the liquid bridge (see text for details).