

Supplementary Information to:

Effect of temperature on the viscoelastic properties of nano-confined liquid mixtures

Kislon Voitchovsky

Durham University, Physics Department, Durham DH1 3LE, UK

email: kison.voitchovsky@durham.ac.uk

Content

- Supplementary Methods (Fig. S1)
- Shear amplitude and phase for all temperatures: Squalane (Fig. S2)
- Shear amplitude and phase for all temperatures: Hexadecane (Fig. S3)
- Variability of the shear data in Sq3:1Hd (Fig S4)
- Variability of the shear data in Sq1:1Hd (Fig S5)
- Supplementary References

Supplementary Methods

The cantilevers used for this study (ArrowUHF-AUD) are triangular (Fig S1a), which makes torsional calibration challenging. Existing calibration methods based on non-contact torsional spectra¹⁻⁴ assume a rectangular beam whose length is much larger than its width. This does not apply here and it is *a priori* unclear how the methodology can be adapted, or the error estimated. A variety of methods have been developed for torsional calibration of cantilevers⁵ but they are rarely straightforward to implement. Here two different methods have been used to calibrate the torsional inverse optical lever sensitivity (InvOLS) of the cantilever: (i) the non-contact thermal method²⁻⁴ and (ii) a direct geometrical method involving scanning across a vertical step⁶.

The thermal method is based on the fitting the torsional thermal spectrum of the cantilever (Fig. S1b) with a Lorentzian⁷ so as to derive the resonant frequency and Q-factor of the first torsional mode and the power spectrum density of the photodetector at DC. The methodology is described in detail elsewhere³. It is also necessary to know the torsional torque constant which can be calculated from the cantilever's dimensions for rectangular levers^{2,3}. The values of InvOLS and torsional spring constant derived by this method are given below for different cantilever widths, always assuming a rectangular beam with length given in Fig. S1a.

Assumed cantilever width [μm]	InvOLS [nm/Volt]	Torsion spring constant [N/m]
40.5	70	493
30	107	210
20	188	68
10	465	11

The thermal spectra were acquired in air at 25 °C. The air density and viscosity were taken as 1.18 kg/m³ and 1.98×10⁻⁵ Pa s respectively. Comparison with the vertical step method indicates that the results obtained for an assumed cantilever width of 30 μm are the most accurate. This suggests an effective torsional spring constant close to 200 N/m.

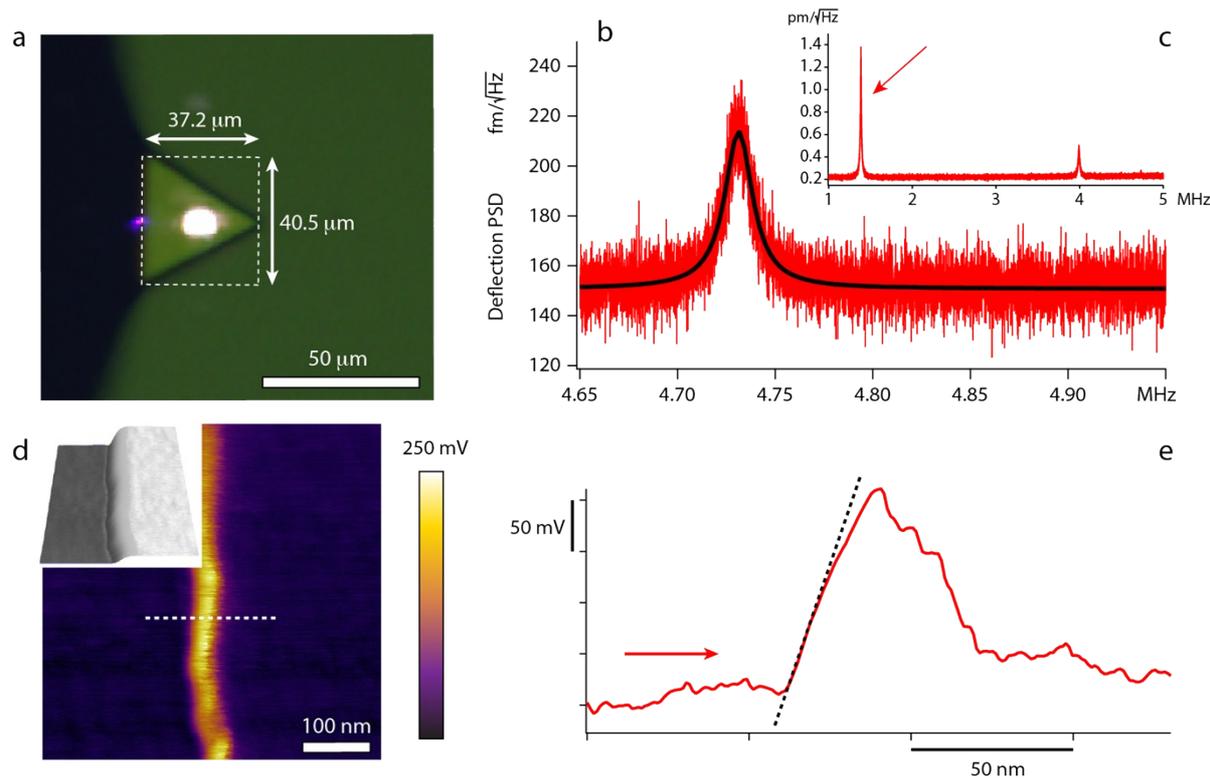


Fig S1 Torsional calibration of the cantilever inverse optical lever sensitivity. The cantilevers used of this study are triangular (a). The torsional thermal spectrum acquired in air (b) show a resonance peak at ~ 4.73 MHz with a Q-factor of ~ 300 . The fit used to calculate the InvOLS and torsional spring constant is also shown (black). For comparison, the normal deflection thermal spectrum (c) shows a peak near ~ 1.3 MHz (first eigenmode, arrow). The second eigenmode is also visible at ~ 4 MHz. A crude estimate of the torsional InvOLS can be obtained by scanning side-ways a vertical step (here 17 nm high) in contact mode with minimal imaging feedback (d-e). Using low gains (<1) delays the feedback, inducing a substantial torsion of the cantilever crossing the step (d). The topographic image (inset in grey scale) exhibits a rounded step, confirming the slow reaction of the feedback. A section across the torsion signal (dotted line in d) is reproduced in (e). As the tip meets the step the torsion initially increases linearly (dotted black line) while the tip twists before the feedback reacts. Given the small height of the step (compared to the $3 \mu\text{m}$ tip height), the slope of the dotted black line provides a direct estimate of the torsional InvOLS, here ~ 110 nm/Volt. The red arrow in (e) shows the scan direction of the moving tip.

The vertical step method measures the cantilever torsion induced by the tip scanning a vertical step. In principle the geometry of the tip, the height of the step and the applied force need to be taken into consideration in order to calculate the InvOLS⁶. Here the problem is simplified by considering a step 17 ± 1 nm high (TGZ 1 calibration grid, Ted Pella Inc), comparable to the size of the tip radius. The step is scanned in contact mode at 90° (laterally) with a minimal feedback loop. Here a feedback gain of about 5% of the normal working value was used while maintaining an important normal force (~ 20 nN) and a relatively fast scanning speed ($3.5 \mu\text{m/s}$). Under these condition, when the tip travelling horizontally meets the bottom of the step, the feedback is too slow to react immediately and the tip get initially stuck at the step, inducing a twist of the cantilever. The twisting is directly measurable in the lateral signal of the photodiode (Fig. S1d). The height of the step being very small compared to the tip height ($3 \mu\text{m}$), it is reasonable to assume that the tip is effectively pinned by its apex at the step as the cantilever twists. A linear fit of this initial twisting phase (Fig. S1e) provides a direct estimate of the torsional InvOLS. Here, a value of ~ 110 nm/Volt was consistently found, regardless of small variations in scan speed and feedback gain. For comparison, a typical deflection InvOLS for the same cantilever yields values around 20 nm/Volt.

Shear amplitude and phase for all temperatures: Squalane

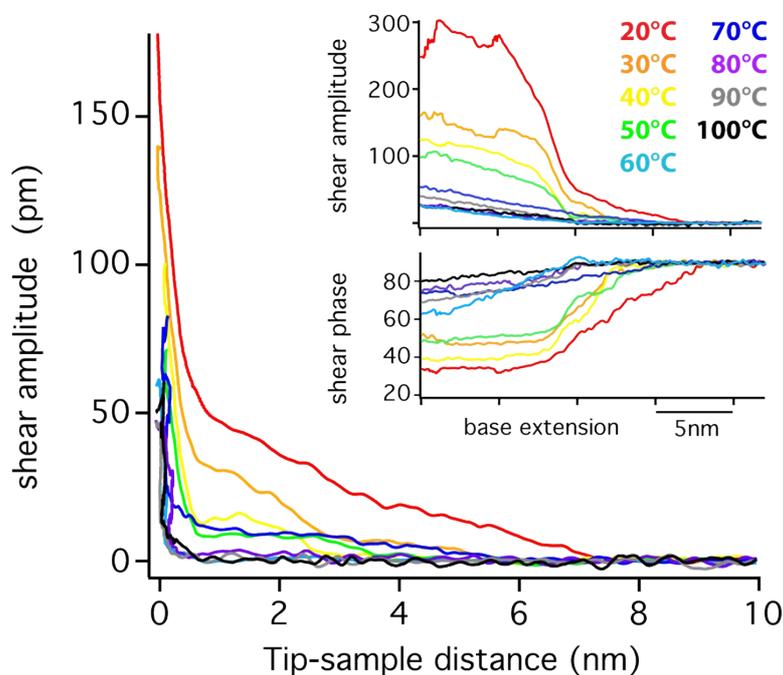


Fig S2 Evolution of the shear amplitude and phase in pure Sq as a function of temperature. Each curve is an average over more than 100 force curves acquired over different locations of the interface. The shear amplitude increase as a function of the true tip-sample distance is given in (a) with the averaged raw data (as acquired) given in inset. The ‘true’ tip sample distance is based on the vertical deflection of the cantilever as it approaches the surface. The amplitude increases already ~ 8 nm away from the surface at 20°C, providing an indication of the thickness of the adsorbed Sq-based layers. At higher temperatures ($>70^\circ\text{C}$) no substantial increase is observed. A temperature evolution is visible in both amplitude in phase, with in both cases a convergence towards a similar behaviour at higher temperatures. The overall temperature evolution is consistent with the image observations of a cohesive Sq layers on the surface (Fig. 4). Generally, the shear force curves were always reproducible until 60°C regardless of location. Past 60°C the main surface layer ‘melts’ leaving different types of molecular coverage and more variability between results acquired over different locations of the sample.

From the data, it is in principle possible to calculate the changes in effective liquid viscosity and storage/loss moduli of the confined liquid^{8,9}. However, such calculations rest on knowledge of the torsion stiffness of the cantilever and of the liquid slippage boundary conditions¹⁰ at the interface with the HOPG. Given the uncertainty on both counts, this data has not been calculated here. The slippage conditions, in particular, would be difficult to implement given their high variability with temperature: at lower temperatures the presence of structured, stagnant interfacial layers (Fig. 6) imply negative slip length while at higher temperatures the slip lengths are clearly positive. Considering only orders of magnitude, the current data indicates an increase of more than 4 orders of magnitude of the effective viscosity of the sheared liquid.

Shear amplitude and phase for all temperatures: Hexadecane

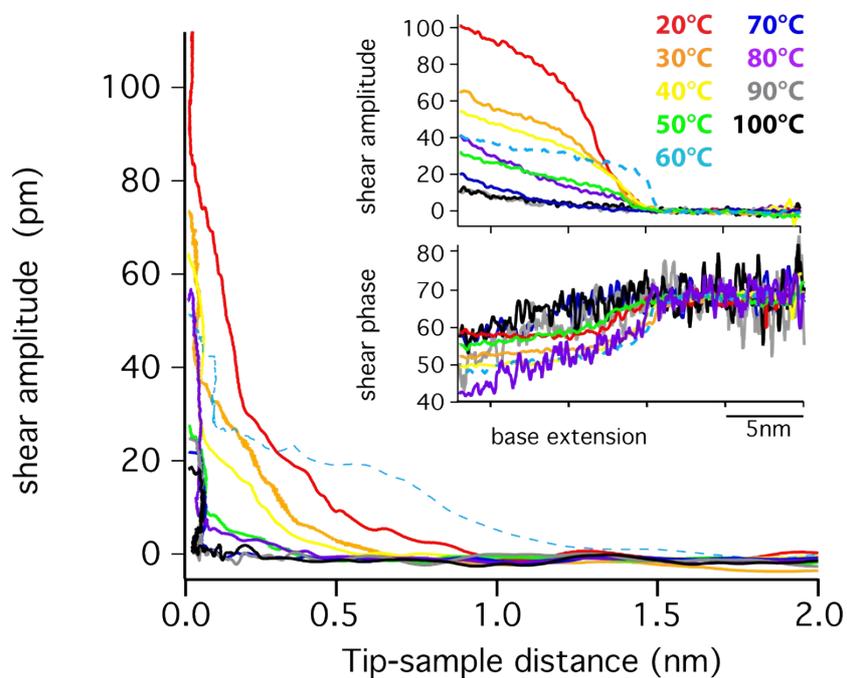


Fig S3 Evolution of the shear measurements with temperature in Hd. The shear amplitude increase as a function of the true tip-sample distance is given in (a) with the averaged raw data (as acquired) given in inset. An amplitude increase is only measured for confining distance $<1\text{nm}$ at 20°C . Most of the evolution with temperature is observed in the amplitude with little change in the phase; the confined liquid remains largely viscous. At higher temperatures, the phase becomes noisier despite the averaging due to the vanishingly small shear amplitudes. Overall, the temperature evolution is consistent with a more fragile and viscous interface where the tip can squeeze out all the confined liquid at higher enough pressure/temperature this is also in agreement with high-resolution imaging (Fig. 6) where the AFM tip was shown to remove all the Hd molecules between the HOPG and the tip at 90°C .

Variability of the shear data in Sq3:1Hd

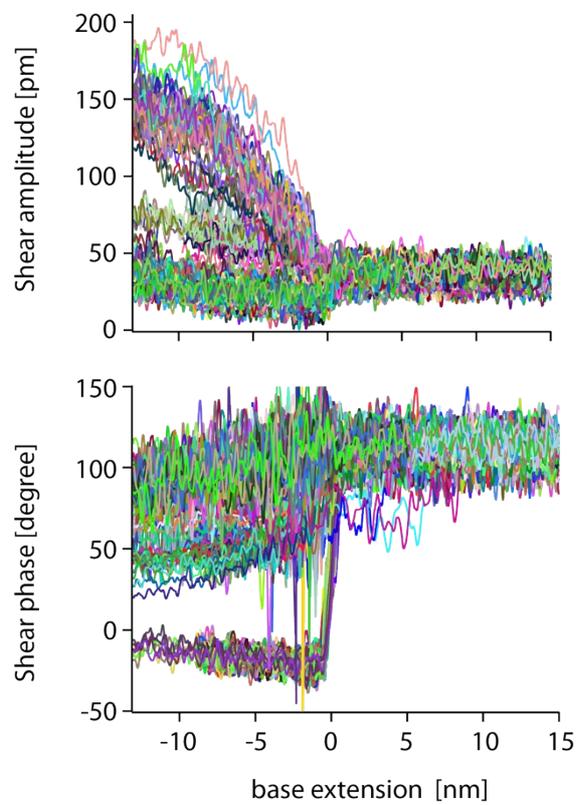


Fig S4 Example of variability in the shear amplitude and phase measured in the Sq3:1Hd at 70 °C. All the curves (>100) were taken individually in a same measurement and with a same tip over different locations. Given the large number of curves, a traditional display is given (as opposed to true tip-sample distance). Two main trends are visible both in phase and amplitude.

Variability of the shear data in Sq3:1Hd

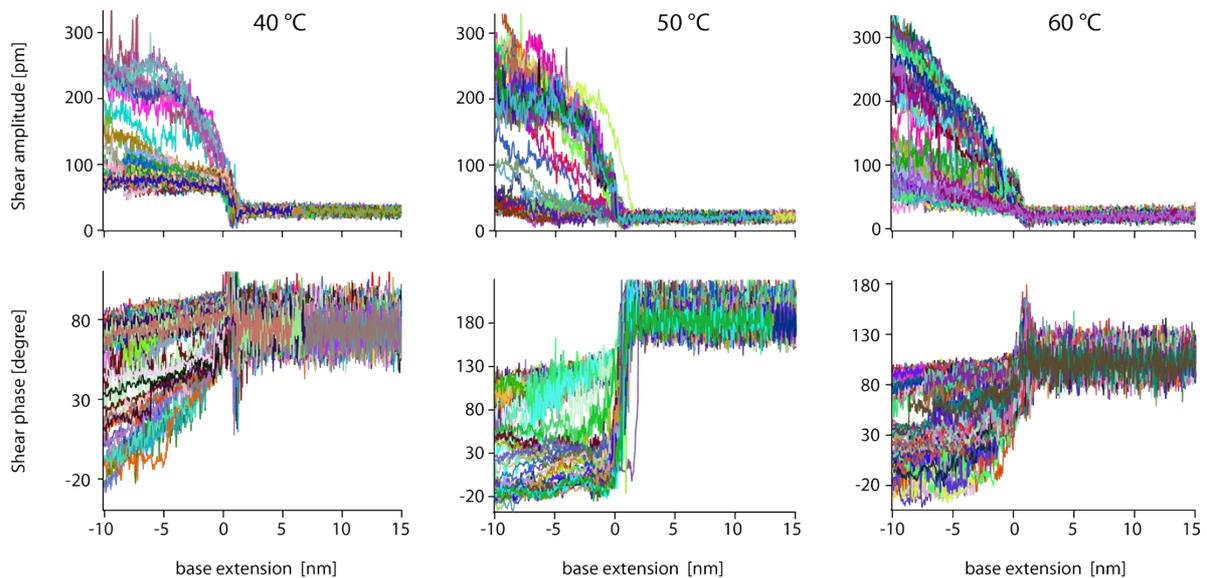


Fig S5 Example of variability in the shear amplitude and phase measured in the Sq1:1Hd at 40 °C (a), 50 °C (b) and 60 °C (c). In each case more than 100 curves are shown, taken individually in a same measurement and with a same tip over different locations. Given the large number of curves, a traditional display is given. Multiple trends are visible at each temperature probed both in phase and amplitude.

Supplementary References

- 1 C. P. Green and J. E. Sader, *J. Appl. Phys.*, 2002, **92**, 6262–6274.
- 2 C. P. Green, H. Lioe, J. P. Cleveland, R. Proksch, P. Mulvaney and J. E. Sader, *Rev. Sci. Instrum.*, 2004, **75**, 1988–1996.
- 3 N. Mullin and J. K. Hobbs, *Rev. Sci. Instrum.*, 2014, **85**, 113703.
- 4 K. Wagner, P. Cheng and D. Vezenov, *Langmuir*, 2011, **27**, 4635–4644.
- 5 M. Munz, *J. Physics D: Appl. Phys.*, 2010, **43**, 063001.
- 6 D. Choi, W. Hwang and E. Yoon, *J. Microsc.*, 2007, **228**, 190–199.
- 7 J. L. Hutter and J. Bechhoefer, *Rev. Sci. Instrum.*, 1993, **64**, 1868–1873.
- 8 T.-D. Li and E. Riedo, *Phys. Rev. Lett.*, 2008, **100**, 106102–106104.
- 9 D. Ortiz-Young, H. C. Chiu, S. Kim, K. Voitchovsky and E. Riedo, *Nat. Commun.*, 2013, **4**, 2482.
- 10 T. Schmatko, H. Hervet and L. Léger, *Phys. Rev. Lett.*, 2005, **94**, 244501.