Supporting Information for

Highly Spherical Nanoparticles Probe Gigahertz Viscoelastic Flows of Simple Liquids Without the No-Slip Condition

Brian Uthe,[1] Jesse F. Collis,[2] Mahyar Madadi,[2] John E. Sader[2,‡] and Matthew Pelton[1,]*

[1]Department of Physics, UMBC (University of Maryland, Baltimore County), Baltimore, MD 21250, USA

[2] ARC Centre of Excellence in Exciton Science, School of Mathematics and Statistics, The University of Melbourne, Victoria 3010, Australia

**mpelton@umbc.edu*

[‡] jsader@unimelb.edu.au

A. Sample preparation

Highly monodisperse, highly spherical 50 nm diameter nanospheres capped with PEG-carboxyl are purchased from nanoComposix; the sample as purchased is suspended in an aqueous 2 mM sodium citrate solution. The as-purchased nanosphere solution is dispensed into 1.5 mL tubes and centrifuged at 8500 g and 20 °C for 10 minutes. The supernatant is then decanted and the pellet resuspended with nanopure water. The solutions for the optical measurements are formed by mixing different mass concentrations of the now suspended nanoparticles in water and glycerol, such that the optical density of the plasmon resonance of the solution contained in a 2-mm cuvette is between 0.25 and 0.35 (see Figure S1).

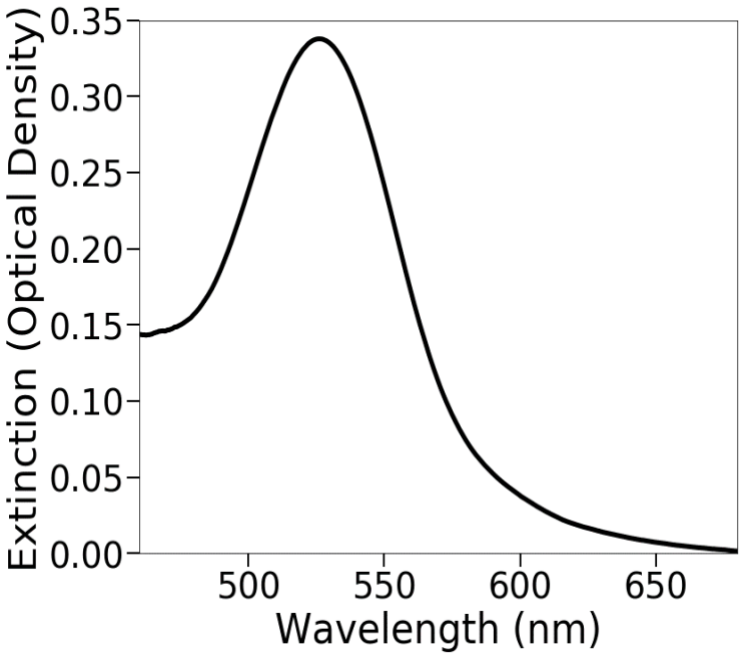

Figure S1. Linear extinction spectrum for an ensemble of highly spherical gold nanospheres suspended in water.

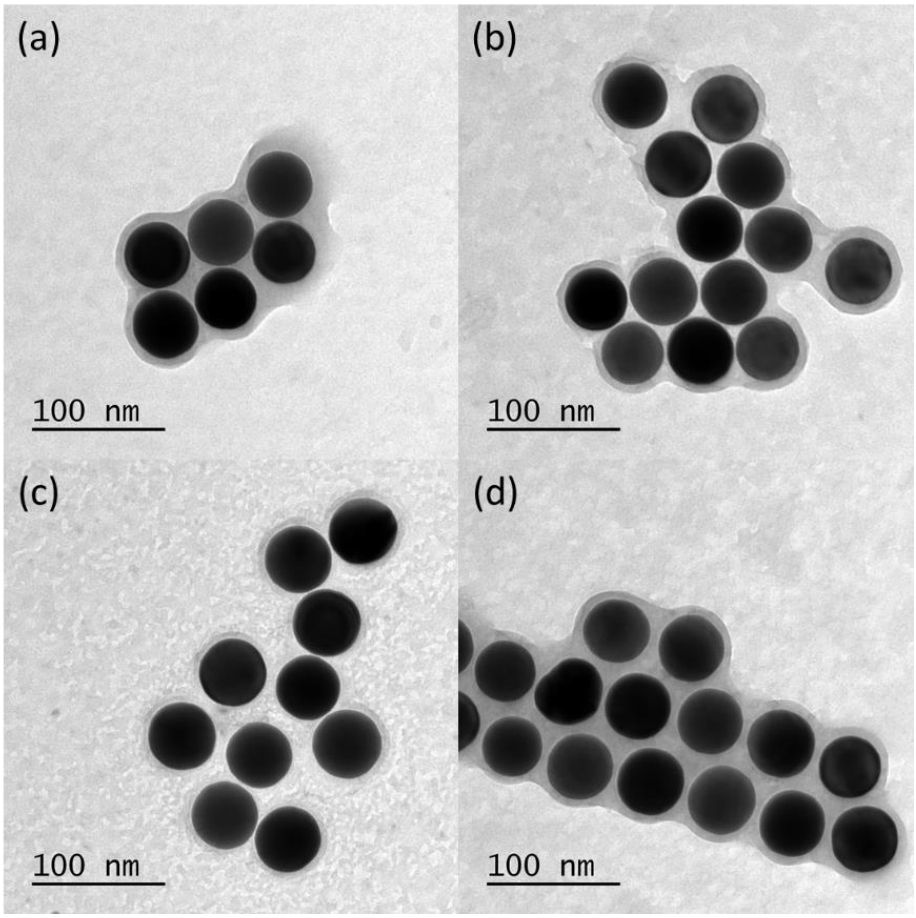

Figure S2. Highly spherical and monodisperse nanoparticle sample. (a-d) Representative transmission-electron-microscope images of the nominally 50-nm diameter nanospheres purchased from nanoComposix. Scale bar equals 100 nm.

B. Transient-absorption measurements and data analysis

Measurements are performed following refs 1-3. A suspension of spherical gold nanoparticles is excited with a pump laser tuned to their plasmon resonance. Absorption of pump laser light by the nanospheres leads to their rapid heating and expansion; this, in turn, impulsively excites coherent acoustic oscillations of the nanoparticles. The resulting periodic changes in the shape and size of the nanoparticles as well as varying strain within the nanoparticles all result in oscillation of the plasmon frequency. This oscillation is detected through the changes it produces in the

transmission of a time-delayed probe pulse. The frequency and decay rate of the oscillating signal give the quality factor for the nanoparticle vibrations.

Measurements are performed using an Ultrafast Systems Helios spectrometer. Pump and probe laser pulses are derived from a regeneratively amplified Ti:Sapphire oscillator (Spectra Physics Tsunami/SpitfirePro) operating at 2 kHz. A 90:10 beam splitter is then used to create the pump pulse (90%) and the probe pulse (10%) from the amplifier output. The probe pulse travels along a path with a delay line to control when it arrives at the sample in relation to the pump pulse. Before the sample, the probe pulse passes through a sapphire plate to generate a continuum, which is then focused to a point inside the sample cuvette. The transmitted light is coupled into an optical fiber and passed to a spectrometer.

Six spectra at negative pump-probe laser pulse delay times, corresponding to the probe pulse arriving before the pump pulse, are averaged and subtracted from all remaining spectra. The corrected transient extinction spectra are fitted, for each time delay, to a difference of Lorentzian functions using a non-linear least squares technique. This is used to determine the plasmon resonance peak position at each delay time.

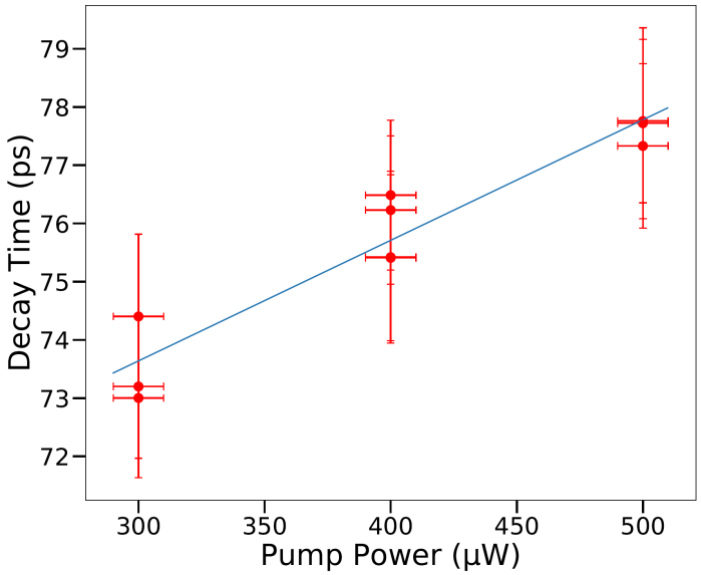

Figure S3. Representative fit parameters obtained from analysis of the transient-absorption data. At least three measurements (red circles; error bars represent a 95% confidence interval) were performed at each of three different average pump powers and an orthogonal linear distance regression (blue line) was performed on the fit parameters to obtain the frequency and decay time of the nanoparticle vibrations at zero pump power. The quality factor is determined from the zero pump power parameters.

From this, the fractional peak shift as a function of time is fitted to a model of a damped oscillation on a decaying background using the same non-linear least squares fitting routine. We begin the fit at a delay time of approximately 20 ps to ensure that changes in the spectra are a result only of the vibrations of the nanoparticle.

The fitted decay time and oscillation frequency are dependent on the incident pump power. At least three measurements were performed at each of three different average pump powers and an orthogonal distance regression linear extrapolation is performed to obtain values for zero incident pump power, as shown in Figure S3. The resulting zero-power decay times and frequencies are used to determine the quality factors that are then compared to theory.

C. Conventional nanosphere sample analysis

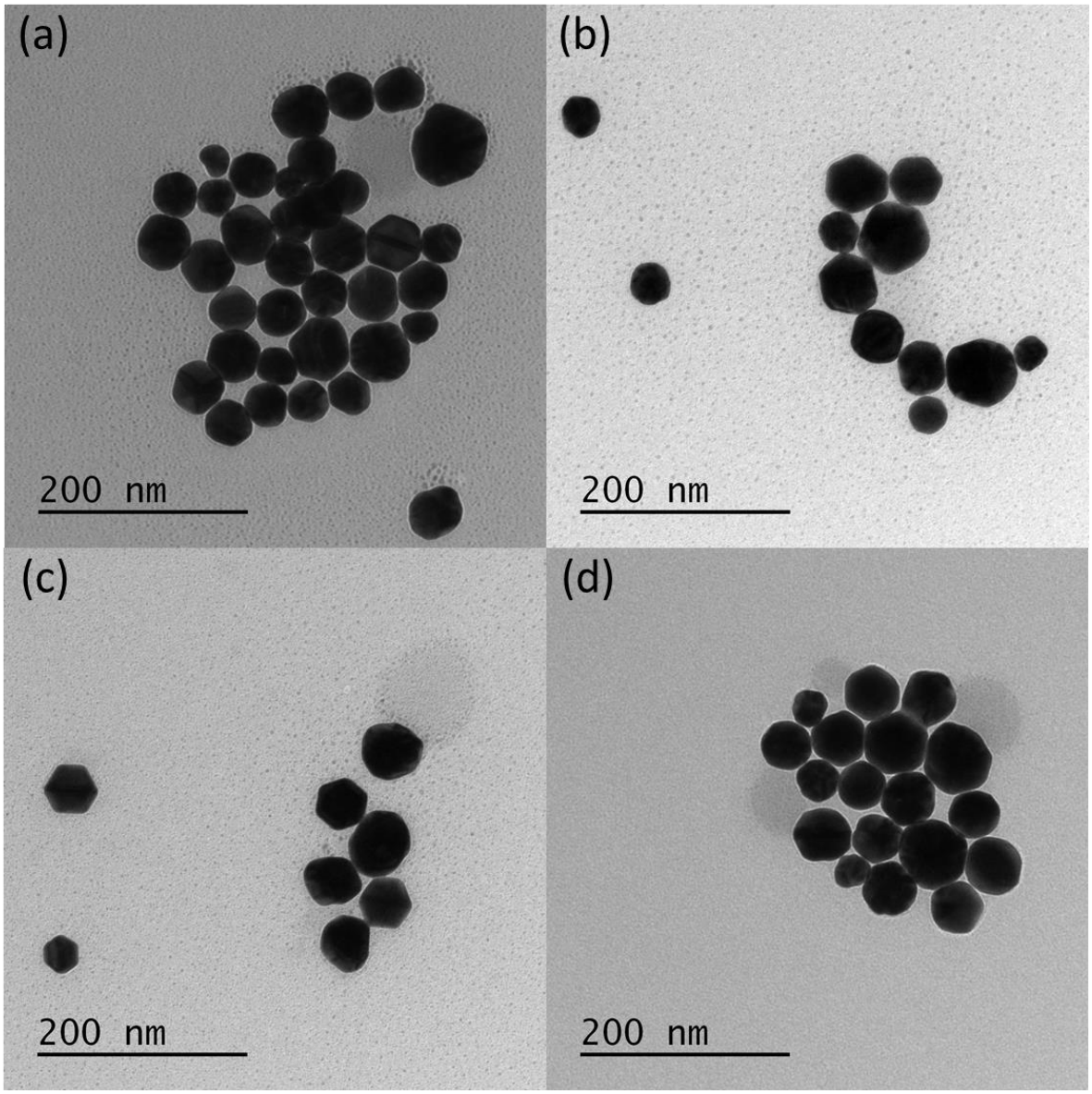

Figure S4. Conventional sample of spherical gold nanoparticles. (a-d) Representative transmission-electron-microscope images of the nominally 50-nm diameter gold nanospheres purchased from Sigma Aldrich. Scale bar equals 200 nm.

D. Ratio of shear to compression Deborah numbers

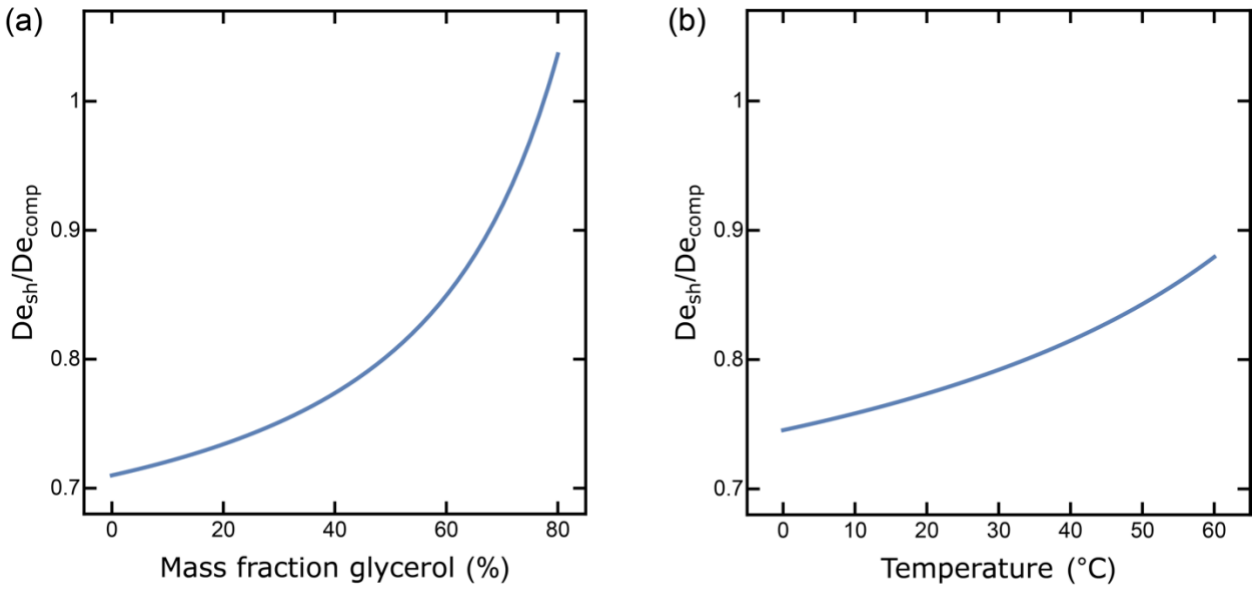

Figure S5. Ratio of shear to compression Deborah numbers as a function of (a) mass fraction glycerol (at constant temperature of 20°C) and (b) temperature (for constant mass fraction glycerol of 40%). Note that purely radial vibrations in a viscoelastic liquid probe both shear and compressional relaxation effects in the liquid and hence both shear and compressional Deborah numbers are needed to characterize this flow.

References

1. Pelton, M.; Chakraborty, D.; Malachosky, E.; Guyot-Sionnest, P.; Sader, J. E. Viscoelastic flows in simple liquids generated by vibrating nanostructures. *Phys. Rev. Lett.* **2013**, *111*, 244502.

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