Electronic Supplementary Material (ESI) for Soft Matter.
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Supplementary Information for

# Non-monotonic Dependence of Pickering Emulsion Gel Rheology on Particle Volume Fraction

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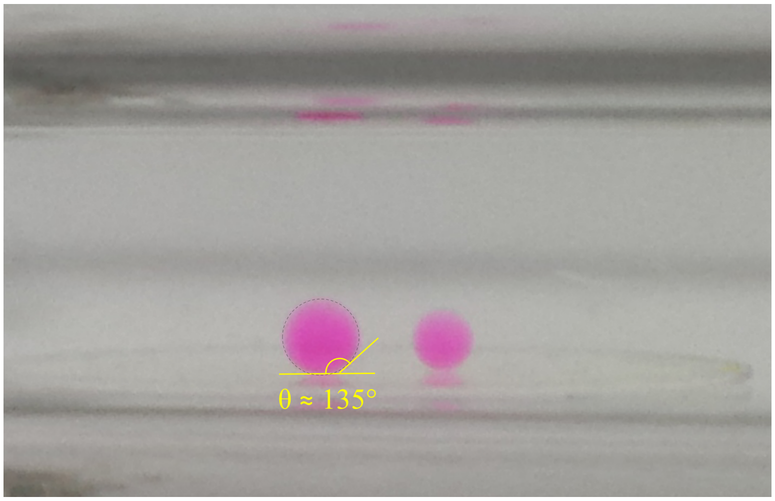

**Figure S1**. The equilibrium three-phase contact angle measured by the immersed droplet method. The aqueous droplet sits on a microscopic slide, drop-coated with silica particles, within the organic fluid phase.

## Derivation of Equation 1 of main text.

From geometric arguments, the volume of spherical particles, $V_{Pt}$, in an ordinary emulsion can be directly related to the number of particles, $n_P$, with diameter $\delta_P$, as shown in Equation A1.

$$V_{Pt} = n_P \frac{4\pi}{3}\left(\frac{\delta_P}{2}\right)^3 \qquad \text{(A1)}$$

The diameter of the particles, $\delta_P$, can be determined experimentally by conducting scanning electron microscopy. The number of particles, $n_P$, within the emulsion however, is found by considering particle packing on the droplet surfaces, which is assumed to follow circle packing on a flat interface. If the particles are taken to pack in a hexagonal close pack arrangement, the available interfacial area, $A_D$, is related to the number of droplets, $n_D$, with diameter $\delta$.

$$A_D = \frac{\pi}{2\sqrt{3}} n_D 4\pi \left(\frac{\delta}{2}\right)^2 \qquad \text{(A2)}$$

Note that Equation A2 assumes particles exhibit a contact angle θ = 90°, which is not the case in our experimental system. In our study, particles with θ > 90° are used to prepare Pickering emulsion gels with a known dispersed fluid volume, $V_D$. The resulting samples can analyzed by confocal microscopy to determine the droplet diameter, $\delta$. This measured droplet diameter can be used to relate the number of droplets, $n_D$, to the total dispersed fluid volume using the same arguments of Equation A1. It cannot be used in Equation A2 as the diameter at which particles will sit on the droplet interface, however. An effective diameter, $\delta_\theta$, is required, that accounts for the fact that partially hydrophobic particles will protrude into the continuous phase at the droplet interface. This protrusion results in a greater effective diameter at which particles cover the fluid droplets in a hexagonal close packed arrangement. Equations A3 and A4 relate the difference between the measured droplet diameter, $\delta$, and the effective diameter, $\delta_\theta$,which is illustrated in Figures A3 and A4.

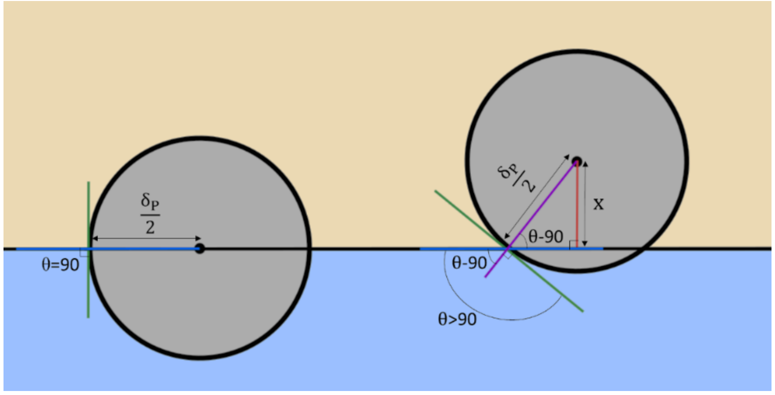

**Figure S2**. An illustration of how a neutral wetting particle, left, sits at the fluid interface versus how a partially hydrophobic particle sits at the fluid interface, right.

$$x = \frac{\delta_P}{2}\sin(\theta - 90) \qquad \text{(A3)}$$

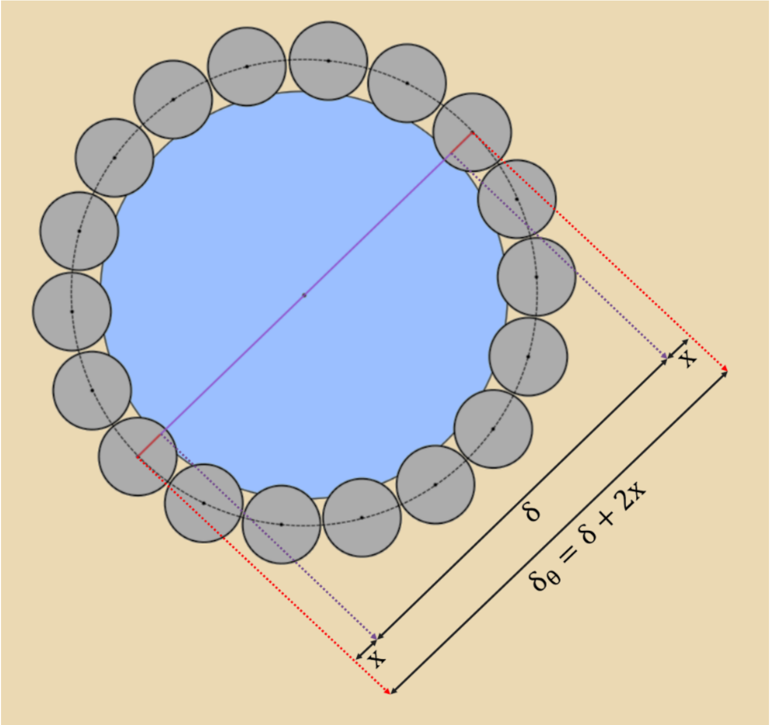

**Figure S3**. An illustration of how particles with θ > 90° pack at an effective droplet diameter, $\delta_\theta$, which is related to the measured droplet diameter, $\delta$.

$$\delta_\theta = \delta + 2x \tag{A4}$$

Accounting for the particles' partial hydrophobicity and expressing the number of droplets, $n_D$, in terms of the total dispersed fluid volume, $V_D$, and the measured droplet diameter, $\delta$, Equation A2 can be rewritten as follows.

$$A_\theta = \frac{3\pi}{\sqrt{3}} V_D \frac{\delta_\theta^2}{\delta^3} \tag{A5}$$

Here, $A_\theta$, gives the actual interfacial area available in the system for particles to cover. In an ordinary Pickering emulsion with fully covered droplets, this area will be equal to the area particles can cover, $A_P$, which is related to number of particles, $n_P$, and their diameter, $\delta_P$.

$$A_P = n_P \pi \left(\frac{\delta_P}{2}\right)^2 \tag{A6}$$

By setting the two areas, $A_\theta$ and $A_P$, equivalent to each other, the number of particles, $n_P$, can be expressed in terms of known or measurable variables, as seen in Equation A7.

$$n_P = \frac{12}{\sqrt{3}} \frac{V_D \delta_\theta^2}{\delta^3 \delta_P^2} \tag{A7}$$

Equation 1 of the main text is now derived by substituting the result of Equation A7 back into Equation A1. Here $V_{Pt}$ gives the theoretical volume of particles with diameter $\delta_P$ and θ > 90° that is required to fully cover droplets with diameter $\delta$ in an ordinary Pickering emulsion prepared with a known dispersed fluid volume, $V_D$.

$$V_{Pt} = \frac{2\pi}{\sqrt{3}} \frac{V_D \delta_P \delta_\theta^2}{\delta^3} \tag{A8}$$

Note, if particles are neutral wetting, θ = 90, then the effective diameter, $\delta_\theta$, is equal to the droplet diameter, $\delta$, and Equation A8 collapses to what has been seen previously in literature.

$$V_{Pt} = \frac{2\pi}{\sqrt{3}} \frac{V_D \delta_P}{\delta} \tag{A9}$$

### Non-dimensionalization of combined variable, $\phi_P/(\delta_P * \phi_D)$.

The combined variable introduced to capture changes made to the formulation of Pickering emulsion gels can be non-dimensionalized by multiplying it by a droplet diameter. Here we show that multiplying by the initial droplet diameter, $\delta_0$, in the formation of a Pickering emulsion gel, yields a variable, $K$, which is effectively the surface coverage of the initial population of droplets.

$$\kappa = \frac{V_P \delta_0}{V_D \delta_P} \tag{A10}$$

We start with $\kappa$, which is equal to the combined variable multiplied by $\delta_0$, but can be rewritten by using Equations A1 for expressions of $V_P$ and $V_D$. The result of substituting these expressions in for $V_P$ and $V_D$ is shown below.

$$\kappa = \frac{n_P \delta_P^2}{n_D \delta_0^2} \tag{A11}$$

The number of particles, $n_P$, and particle diameter, $\delta_P$, can be related to the interfacial area that they can cover, $A_P$, through Equation A6. Similarly, Equation A2 relates the total interfacial area available for particles to cover in a hexagonal close packed arrangement, $A_\theta$, to the number of droplets, $\mathrm{n_D}$, and droplet diameter, $\delta_0$. Employing Equations A6 and A2, we arrive at the following expression for $\kappa$.

$$\kappa = \frac{2\pi}{\sqrt{3}}\frac{\mathrm{A_P}}{\mathrm{A_\theta}} \tag{A12}$$

If we let $\mathrm{K} = \kappa\frac{\sqrt{3}}{2\pi}$, the result gives the interfacial area that a volume of particles, $V_P$, with diameter $\delta_\mathrm{P}$ are able to cover, over the total interfacial area available in a population of droplets with diameter $\delta_0$ and a total volume of $V_D$. Here $\mathrm{K}$ is the initial droplet surface coverage.

$$\mathrm{K} = \frac{\mathrm{A_P}}{\mathrm{A_\theta}} \tag{A13}$$

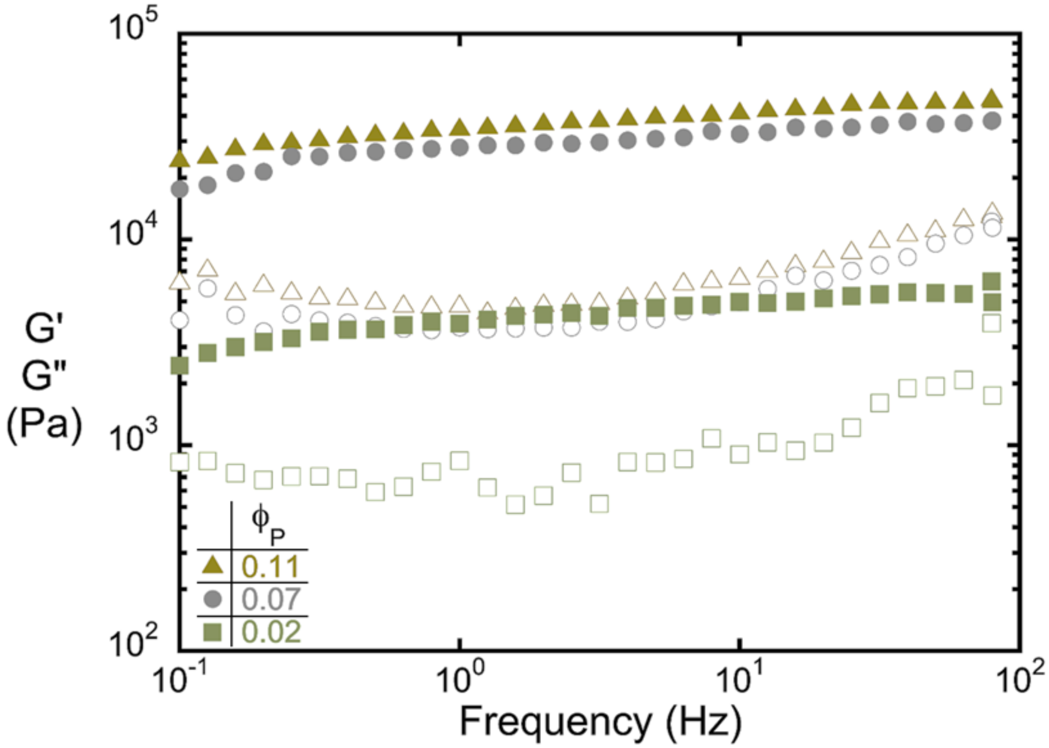

**Figure S4**. Frequency sweep results for the Pickering emulsion gels shown in Figure 3 of the main text.

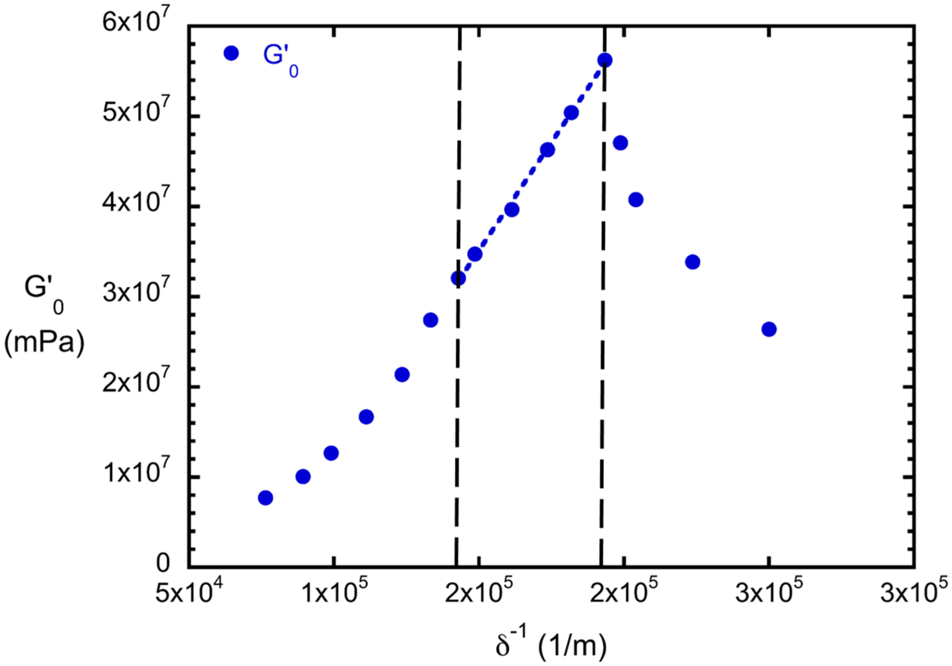

**Figure S5**. G'$_0$ data from Figure 4a of main text is plotted against inverse droplet size, 1/δ. The slope of the linear region between the dashed vertical lines is ~500 mN/m.

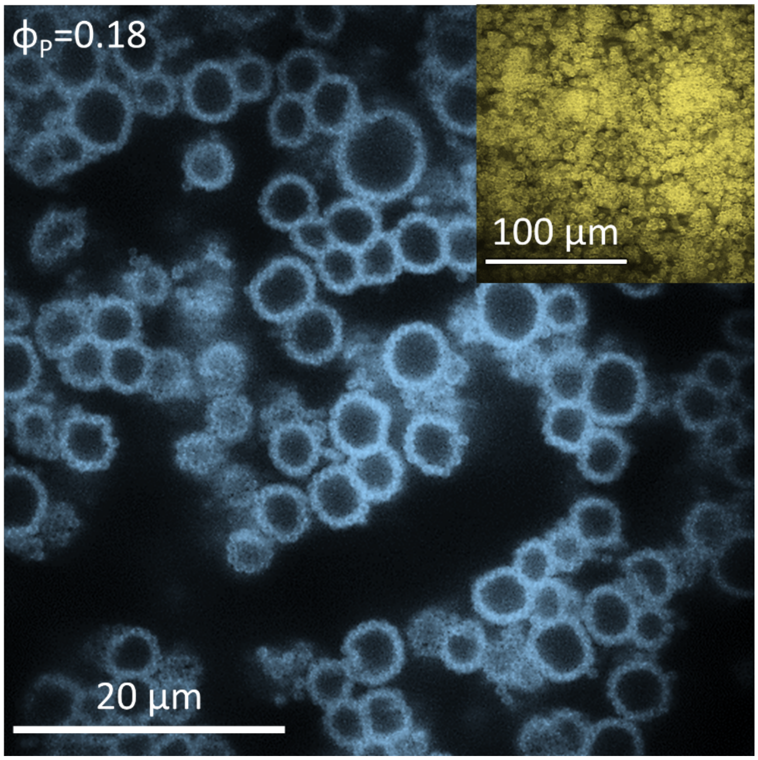

**Figure S6**. Confocal microscopy images of a Pickering emulsion gel created at a high $\phi_P$, where free particles in the continuous phase are evident.

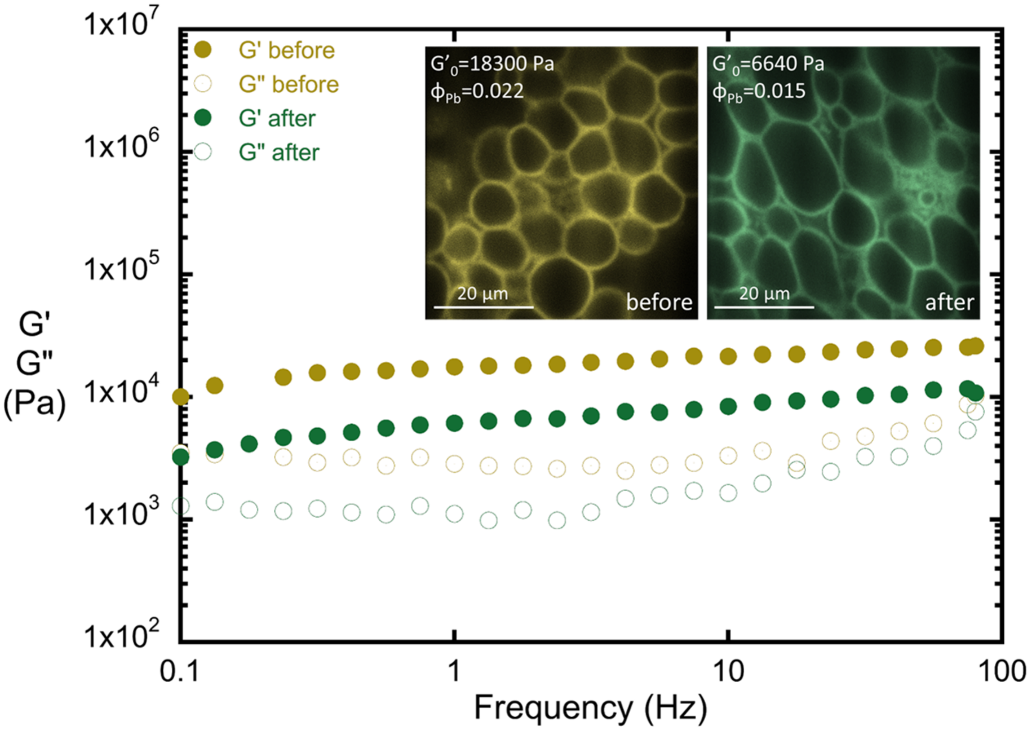

**Figure S7**. Frequency sweeps, done at $\gamma$ = 0.01%, on a Pickering emulsion gel sample, before and after, it underwent a simple shear at a low shear rate of $\dot{\gamma}$ = 50 $s^{-1}$ for 2 minutes. The sample was prepared at $\phi_P$ = 0.05 and $\eta$ = 30/70.

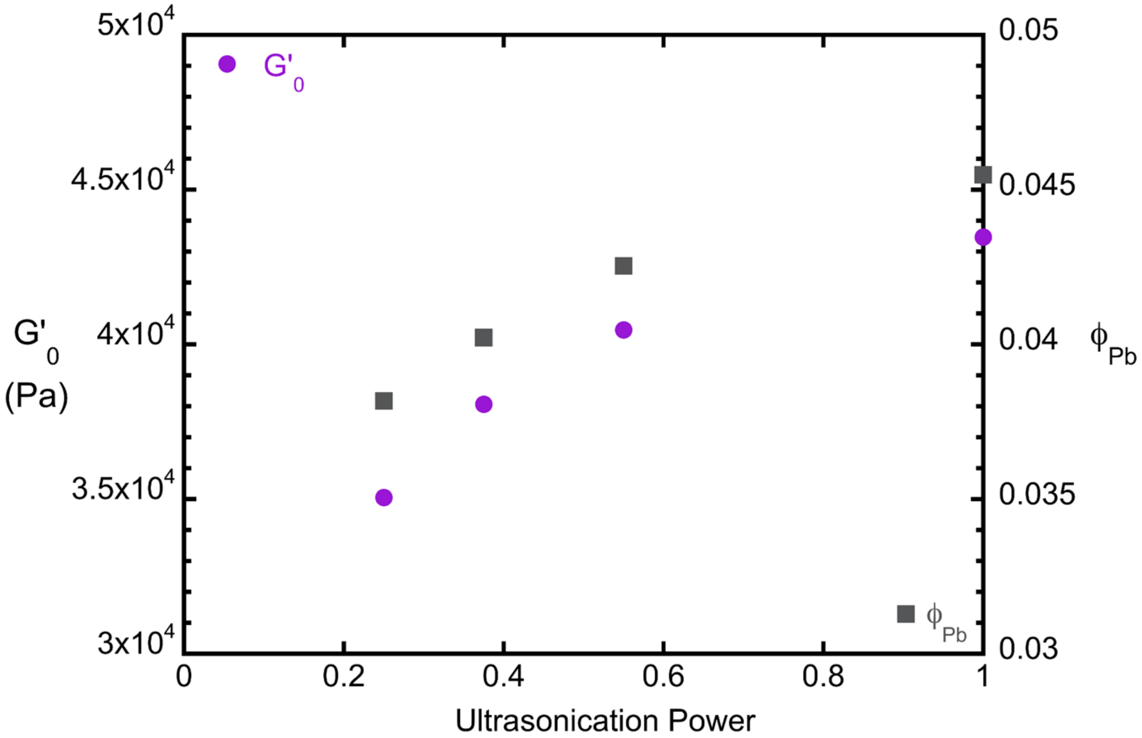

**Figure S8**. $G'_0$ of Pickering emulsion gel samples with the same $\phi_P$ = 0.085 and $\eta$ = 30/70, but formed at different ultrasonication powers. Note that the ultrasonication power was scaled by the greatest power used. On the secondary axis, $\phi_{Pb}$ for each sample is plotted.