Supporting Information for
"Spectroscopic Analysis of Liquid / Liquid Interfaces in Multiphase Microflows"

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Conventional quasi-elastic laser scattering (QELS) method

Quasi-elastic laser scattering (QELS) method is an interfacial-selective measurement method for capillary wave at liquid / liquid or liquid / gas interfaces.[S1-S5]

Principle and an optical setup of conventional QELS measurement are presented in Figure S1. When organic phase contacts with aqueous phase, capillary wave having an amplitude of several angstrom to one nanometer is induced at the aqueous / organic (A/O) interface due to thermal fluctuation. When an incident beam irradiates the interface, the capillary wave having a wave number k scatters the beam, where the relationship of $k = K \sin\theta$ is required from momentum conservation. K is the wave number of the laser light and θ is scattering angle. In the scattering process, the incident light frequency F is modulated by the capillary wave having a frequency of f_0 and, then, the scattered light has a frequency of $F \pm f_0$. By mixing the local beam having frequency of F with the scattered light, the capillary wave frequency f_0 can be measured as a beat frequency. In the conventional setup presented in Figure 1S, an optical grating is used to split the local beam and to determine the scattering angle θ.

The observed beat frequency f_0 can be related to the wave number k and interfacial tension γ as[S6]

$$f_0 = \frac{1}{2\pi}\left(\frac{\gamma k^3}{\rho_A + \rho_O}\right)^{\frac{1}{2}}, \tag{S1}$$

where ρ_A and ρ_O are densities of aqueous and organic phases, respectively, and k is wave number of capillary wave. Therefore, when we measure the frequency f_0, we can discuss the interfacial tension γ. Furthermore, the interfacial tension change due to adsorption of solute chemical compounds can be related to interfacial density (interface excess concentration) Γ. When we know the limit of interfacial density Γ^∞ and Langmuir adsorption model is assumed, Γ can be obtained from $\Delta\gamma$ as

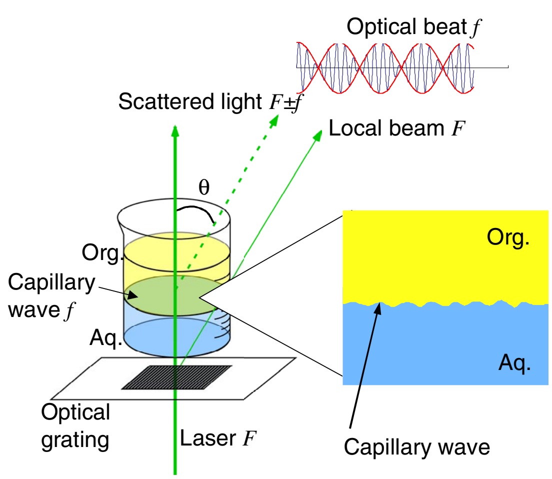

Figure S1 Principle and optical setup of conventional QELS measurements.

$$\Gamma = \Gamma^{\infty}\left(1-\exp\left(-\frac{\Delta\gamma}{RT\Gamma^{\infty}}\right)\right). \tag{S2}$$

Thus, decrease of the beat frequency corresponds to increase of the interfacial density as shown in Figure 2b (in the article).

Microscale quasi-elastic laser scattering (μQELS) method

Although QELS method seems a promising tool for the liquid interface, it is difficult to apply to A/O interface in multiphase microflows (MPMF) in the microchannel because of problems concerning to optical configuration and low frequency noise due to the flow. The scattering angle is important for analysis but it is difficult to determine the scattering angle under a microscope objective lens. Furthermore, the optical beat signal is obtained around 0 Hz (DC) in the conventional method. For the multiphase flow analysis, low frequency noise due to flow fluctuation should be avoided.

In order to satisfy these two requirements, the local beam is split beforehand and the parallel two beams are focused by the objective lens as shown in Figure 1 (in the article). The scattering angle, which corresponds to crossing angle between the incident and local beam, can be determined from a numerical aperture of the objective lens and distance between the two beams. The laser beam is split by an acousto-optic modulator (AOM) working with a center frequency of 80 MHz. The transmitted beam is used as incident beam and the 1st order diffracted beam is used as local beam. The frequency of the local beam is shifted by 80 MHz in the diffraction process and, therefore, the local beam has a frequency F+80 MHz. By mixing the local light with the scattered light having a frequency of $F \pm f_0$, we can measure the beat frequency, 80 MHz$\pm f_0$. Based on conventional QELS theory,[S7] the spectrum shape $P(f)$ can be fitted by

$$\begin{aligned} P(f) \propto\ & \frac{1}{1+\left[(f-f_0)/\Delta f\right]^2} + \frac{1}{1+\left[(f+f_0)/\Delta f\right]^2} \\ & + \frac{\Delta f}{f_0}\left(\frac{(f_0-f)/\Delta f}{1+\left[(f-f_0)/\Delta f\right]^2}\right) + \frac{\Delta f}{f_0}\left(\frac{(f_0+f)/\Delta f}{1+\left[(f+f_0)/\Delta f\right]^2}\right), \end{aligned} \tag{S3}$$

where Δf is damping factor. The solid line in Figure 2a (in the article) shows the fitted result with this equation.

In this article, the liquid interfaces were measured at 10-mm downstream from the junction point. Before determining the measurement point, we confirmed that the beat frequency did not depend on the location from the junction point and that

References

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