THERMAL CHARACTERIZATION OF LIQUID ANALYTES VIA PHOTOTHERMAL MODULATION OF MICROFLUIDIC RESONATORS

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ABSTRACT

This paper reports the first thermal characterization of liquid analytes via photothermal modulation of microfluidic resonators in dynamic mode. Measurements of thermophysical properties of liquid analytes are enabled by real-time tracking of the resonance frequency shift of the microfluidic resonator while the liquid filled resonator is irradiated by a diode laser. The local irradiation induces the photothermal heating of the resonator as well as the loaded liquid sample. The volumetric thermal expansion coefficients of various liquids are correlated with resonance frequency shifts of the resonator and the ratio of specific heat to thermal conductivity tuned by varying the mole fraction of ethanol-water binary mixtures shows linear dependence on the heating time constant. In addition, a higher flexural mode displays improved sensitivity for thermal characterization of liquids via photothermal heating.

INTRODUCTION

Mechanical resonators with integrated fluidic channels have drawn continuous attention and utilized for measuring mass, volume and density of suspended particles [1], and viscosity of liquid analytes with high resolution [2]. In another research, microfluidic cantilevers have been utilized for single cell manipulation under atomic force microscope configuration [3]. Having embedded fluidic channels offers facile loading and unloading of particle suspensions as well as liquid samples in a programmable manner where measurements can be made while suspended particles or liquid samples flow through the channel. Microfluidic cantilevers with integrated channels is additionally useful for thermal property measurements of liquid samples since integrated channels simply behave as a control volume. If proper heating and temperature sensing techniques are added to microfluidic cantilevers, calorimetric measurements for a fixed volume of liquid samples can be enabled.

Previously, microfluidic cantilevers have successfully measured heat capacity of sub-nanoliter volumes of liquids by monitoring static deflection of the cantilever [4]. Although this was the original and inspiring application of microfluidic resonators for thermal property measurements, there were two major drawbacks. One is that a quantum cascade laser (QCL) has been employed for temperature modulation of the measurement system. Another is that the
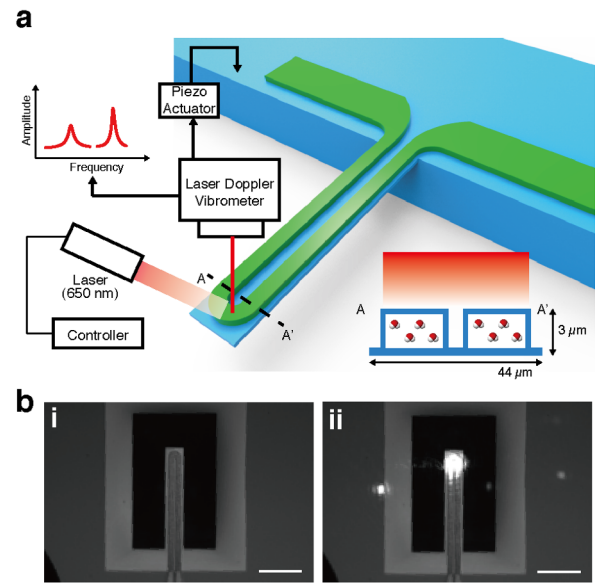

Figure 1: *(a) A conceptual operation schematic of the liquid-loaded microfluidic resonator under photothermal modulation. A laser is used to locally heat up the liquid as well as the resonator. (b) Optical micrographs of the resonator when the heating laser aligned at the free end of the resonator is (i) off and (ii) on. Scale bars are 100 μm.*

temperature indicator of the system was the static deflection resulting from the layered structure with thermal expansion mismatch. Requirement of the QCL definitely prevents the newly demonstrated metrology from being popular and measurements based on static deflection are less reliable during long-term experiments due to the mechanical drift and higher noise level of the photodetector. Therefore, it is necessary to replace the QCL with a more generic light source and to employ an indirect measurement of the system temperature that is less prone to the noise and drift.

In this paper, we report the first thermal characterization of various liquids via photothermal modulation of microfluidic resonators in dynamic mode. Measurements of thermophysical properties of liquid samples are enabled by real-time tracking of the resonance
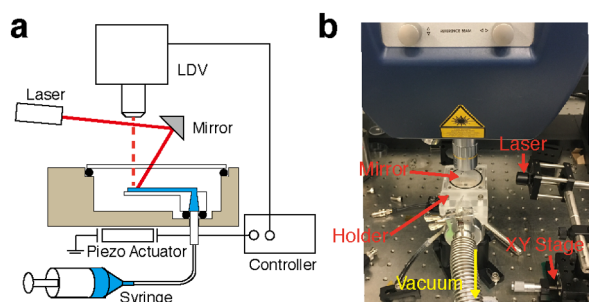
Figure 2: (a) Schematic and (b) photograph of the measurement setup composed of a commercial laser Doppler vibrometer and custom modification for photothermal modulation.

frequency shift of the microfluidic resonator while the liquid filled resonator is irradiated by a diode laser.

METHODOLOGY

Experimental Setup

Figure 1a shows the conceptual operation schematic of the experiment where a silicon nitride microfluidic resonator with a liquid sample is heated by a laser (0.362 mW). The red laser (635 nm) having 20 µm diameter is focused on top of the resonator to locally heat the resonator and liquid analytes within a few milliseconds. The modulation frequency of the laser is controlled by an optical chopper (MC2000B, Thorlabs). The resonance frequency of the resonator is simultaneously measured with a laser Doppler vibrometer (MSA-500, Polytec). Figure 1b shows the resonator with the heating laser off or on, respectively. A detailed schematic and photograph of the experimental setup is shown in Figure 2a and 2b. The resonator is excited by a piezo actuator in vacuum of 3×10^{-5} mbar to offer a high quality factor thus high frequency stability while the integrated channel is at atmospheric pressure or filled with a liquid. Liquid samples are loaded into the integrated microfluidic channel by applying positive pressure with a syringe. Once the measurement is completed, the sample is removed by applying negative pressure with the syringe and the channel is carefully cleaned with deionized water then dried for several
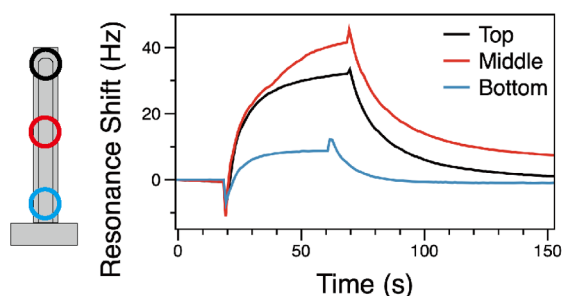

Figure 3: Schematic of the resonator under local photothermal modulation at the free end (black), the mid-point (red), and the clamped base (sky blue) (left) and 1st flexural mode resonance frequency shift of the air-filled resonator under photothermal modulation at three different points (right).
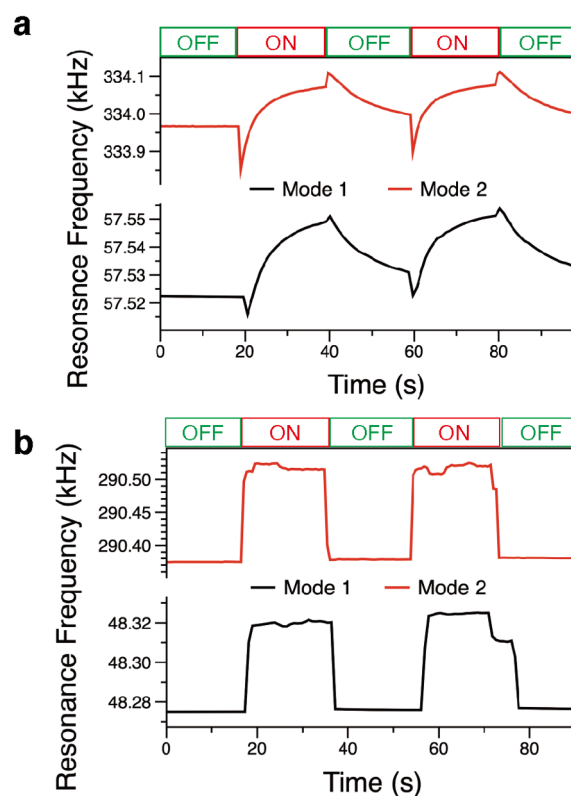

Figure 4: 1st and 2nd flexural mode resonance frequency shifts of the resonator filled with (a) air and (b) water as a result of the photothermal modulation (0.362 mW, 25 mHz, and 50 % duty cycle).

minutes. To enable real time measurement of the resonance frequency of the resonator, an analog feedback circuit is used to oscillate the resonator.

Characterization

The resonance frequency of the air-filled cantilever is characterized by changing the heating laser position on the cantilever (Figure 3). In every case, the resonance frequency instantly drops upon the onset of laser heating and then slowly increases until it becomes saturated. Similarly, the resonance frequency instantly increases and then gradually decreases once the heating laser is off. When the laser is positioned in the middle of the cantilever, the resonance frequency shift of the resonator shows the greatest change, whereas the frequency shift is minimized when the laser is positioned at the bottom of the cantilever.

RESULTS

The resonance frequency of the air-filled resonator is monitored as a function of photothermal modulations (Figure 4a). The labels "OFF" and "ON" indicate the state of the heating laser. In "OFF" state, the laser is blocked by optical chopper whereas the laser is focused on the cantilever in "ON" state. At the onset of "ON" state, the resonance frequency of the air-filled resonator initially decreases and gradually increases. The initial frequency
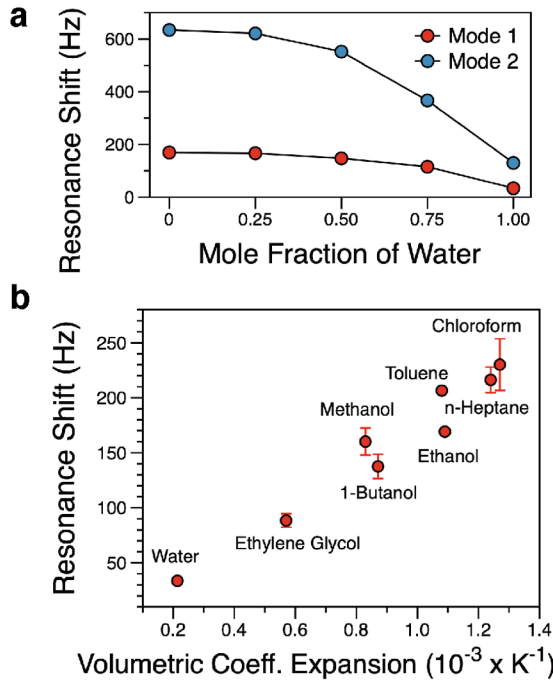
Figure 5: *(a) Saturated 1ˢᵗ and 2ⁿᵈ flexural mode resonance frequency shift of the water-ethanol mixture filled resonator as a function of the mole fraction of water. (b) 1st mode resonance frequency shifts of the resonator filled with different liquids upon the photothermal modulation as a function of volumetric thermal expansion.*

Figure 6: *(a) 1ˢᵗ flexural mode resonance frequency change of the water-filled resonator and its exponential fits for heating and cooling events. (b) Extracted heating time constants for water-ethanol mixtures.*

drop is induced due to the change in Young's modulus of silicon nitride affected from initial heating. The moderate increase of the resonance frequency comes from the density reduction resulting from thermal expansion of air by heating. The resonance frequency of the resonator recovers to the original state once the heating laser turns off. On the other hand, the resonance frequency of the water-filled resonator, however, instantly increases once the heating laser turns on (Figure 4b). In both cases, the frequency shift from the heating is measured for the first two flexural modes of the resonator. As expected, the sensitivity is enhanced with the higher mode.

Resonance shifts of the resonator filled with water-ethanol mixtures in different mole fractions are summarized and compared in Figure 5a. The resonance shift changes in terms of the mixing ratio of different liquids due to the change of thermal properties. The resonance shifts are amplified approximately by 3.8~4.4 times with the 2ⁿᵈ flexural mode. Furthermore, the resonance shifts of the resonator filled with various liquids are plotted as a function of the volumetric thermal expansion coefficient of liquids (Figure 5b). As the volumetric thermal expansion coefficient increases, the resonance shift increases proportionally. As the liquid is heated via photothermal modulation, it expands inside the channel where volume is confined, and eventually, the liquid tends to come out of the channel. This induces the mass reduction within the cantilever that in turn decreases the resonance frequency consequently. This indicates that the liquid sample's volumetric coefficient of thermal expansion can be nicely correlated with the resonance shift.
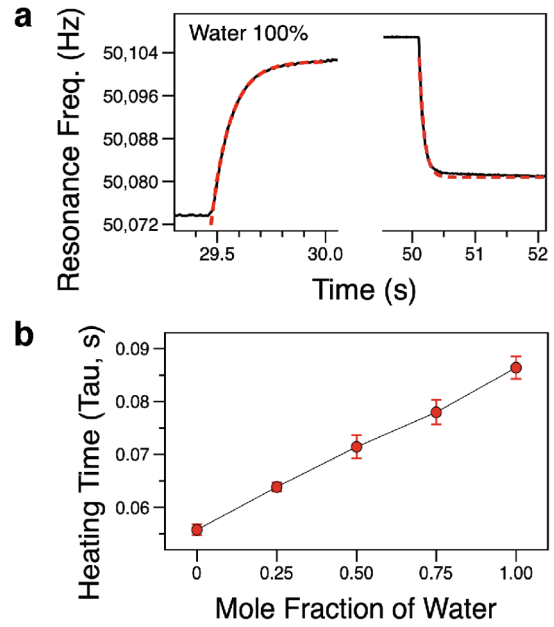
To characterize the transition time associated with the heat transfer within the resonator, exponential fits of the resonator shift upon heating and cooling are compared (Figure 6a). Heating time and cooling time constants of the water-filled resonator are 85.6 ms and 64.0 ms, respectively. The extracted heating time constants for the resonator filled with ethanol-water mixtures are plotted as a function of the mole fraction of water (Figure 6b). The Heating time constant is linearly proportional to the mole fraction of water of ethanol-water mixtures. Table 1 summarizes thermal properties including specific heat, thermal conductivity, and volumetric thermal expansion coefficient [5], and measured resonance frequency shift and heating time constant for various liquid samples.

Table 1. Thermal properties and measured values from the resonator for water, ethylene glycol, ethanol and chloroform.

	Water	Ethylene Glycol	Ethanol	Chloroform
Specific heat (kJ/kg-K)	4.19	2.36	2.46	1.05
Thermal conductivity W/(m-K)	0.607	0.256	0.169	0.119
Volumetric expansion coefficient ($10^{-3} \times K^{-1}$)	0.21	0.57	1.09	1.27
Frequency shift (Hz)	33.57	88.48	169.2	230.2
Heating time constant (ms)	86.7	64.4	55.1	62.8

CONCLUSIONS

In conclusion, we have demonstrated a new way of precisely measuring thermal properties of liquid analytes with a microfluidic cantilever by monitoring its resonance frequency shift. By comparing resonance frequency shifts, thermal characterization of liquid samples is performed, especially in terms of volumetric thermal expansion coefficient. This method can be generally applicable to thermal analysis of various liquid samples. Since it requires extremely small volume, rare and expensive liquid samples are effectively analyzed by our technique.

ACKNOWLEDGEMENT

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