Determination of Viscosity and Density of Supercritical Fluid Mixtures Using Frequency Response of Microcantilevers

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ABSTRACT

Microcantilevers are very good candidates for environmental probing and biological/chemical sensing applications. They have well defined mechanical resonances which are observed within narrow frequency bands. This leads to a high sensitivity in probing effects based on a shift in their resonance frequencies. These effects can be related to the changes in the viscosity or density of the surrounding fluid or addition of mass to the microcantilevers.

In this study, a new experimental setup was developed in order to determine the thermophysical properties of supercritical fluid mixtures by measuring the frequency response of ferromagnetic nickel microcantilevers immersed in the supercritical fluid mixture at high pressures. The setup includes a temperature controlled high-pressure vessel which can operate within a temperature range of 273 – 423 K and a pressure range of 1 – 300 atm. A microchip containing microcantilevers and an electromagnet are placed inside the vessel. The procedure followed for the determination of microcantilevers resonance frequencies involves driving of microcantilevers with AC magnetic field at varying frequencies and detecting of the laser deflections from the driven cantilevers with a quadrant photodiode (QPD).

Resonance frequencies and quality factors as components of frequency response were measured for supercritical CO_2, supercritical N_2 and supercritical mixtures of CO_2 and N_2. The frequencies and quality factors were found to decrease with increasing density. The experimental data were analyzed in the context of the model of cantilever oscillations under the influence of hydrodynamic forces proposed by Sader. This approach is based on solving the equation of motion for a clamped elastic beam subject to hydrodynamic forces of the surrounding fluid. A very good agreement was shown between the experimental data and the model, thus illustrating suitability of the experimental approach for density and viscosity measurements in various supercritical fluid mixtures including measurements in the mixture critical region.

INTRODUCTION

Microcantilevers are very good candidates for environmental probing and biological/chemical sensing applications. They have well defined mechanical resonances which are observed within narrow frequency bands. Frequency response of an oscillating cantilever can be characterized by its resonant frequency, ω_R, and the quality factor of the oscillations, Q-factor [1]. ω_R is defined as the angular frequency at which the maximum amplitude of oscillation is observed. Q-factor quantifies energy dissipation during oscillation. A smaller resonance bandwidth implies a higher Q-factor and, thus, lower losses. The frequency response of a cantilever beam is strongly dependent on the properties of the fluid in which it is immersed. Due to its definite density and viscosity, the fluid exerts hydrodynamic forces which affect the motion of cantilever oscillation. These fluid forces are based upon effective added mass due to the density of the fluid moving along with the cantilever and energy dissipation due to viscous drag in the fluid. Therefore, it may be possible to relate these thermophysical properties of fluids to frequency response of microcantilevers using models. There are several approaches that explain the oscillatory behavior of microcantilevers in viscous fluids. One approach proposed by Sader is based on solving the equation of motion for a clamped elastic beam subject to hydrodynamic forces of the surrounding fluid. Later the complex hydrodynamic functions introduced by Sader were analytically approximated by Maali et al. [2,3] Youssry et al. incorporated these approximations to Sader's model to obtain formulas for density and viscosity from the measured resonant frequency and Q-factor [4]. To investigate density and viscosity of pure fluids, we developed a new experimental set up that measures frequency response of ferromagnetic nickel microcantilevers immersed in supercritical fluids. Successful measurements up to 27 MPa with pure CO_2 and a good agreement of experimental data with Sader's model suggested that the technique may also be applicable to study the thermophysical properties of fluid mixtures [5]. In this study, we investigated the frequency response of microcantilevers in supercritical mixtures of CO_2 and N_2 at high pressures. Resonance frequency and Q-factor values for different compositions of $CO_2 - N_2$ binary mixture were successfully obtained. A good agreement between model and experimental data indicates our experimental approach can be extended to perform density and viscosity measurements for supercritical fluid mixtures. Thus, our technique can be adapted to detect the composition of a specified mixture at high pressures.

MATERIALS AND METHODS

A home-made experimental set up was built to characterize the frequency responses of microcantilevers to determine the thermophysical properties of liquid, gas and supercritical fluids and fluid mixtures (Figure 1). Ferromagnetic microcantilevers made of nickel were produced using microfabrication steps previously reported by Ozturk et al [6]. The cantilevers were attached in Teflon housing with an electromagnetic actuator and placed in a high pressure vessel (TharSFC 05424-4) which can operate within a temperature range of 273 – 423 K and a pressure range of 1 – 300 atm. Two sapphire windows at each face of the vessel enabled monitoring the cantilevers and optical measurement. Temperature control of the vessel was provided with a heating circulator (Polyscience) and monitored with a thermocouple with ±1 K precision, and pressure was monitored with a pressure transducer.

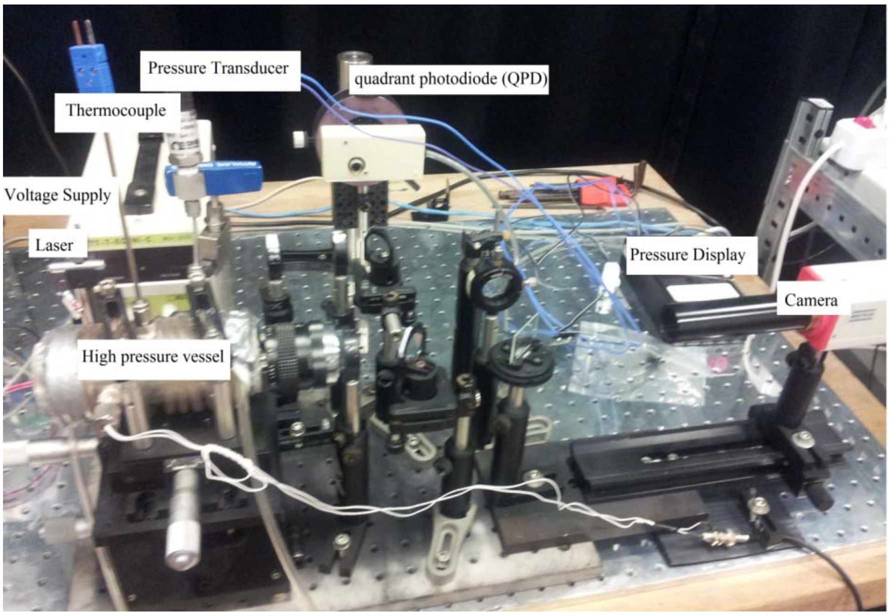

Figure 1: The experimental setup.

The ferromagnetic cantilevers were actuated by AC magnetic field generated by a coil. Sinusoidal output from a function generator (Agilent 33220A) was first amplified 50× by a high-voltage, high-frequency amplifier (Falco Systems WMA-300) before being sent to the coil. A near-infrared laser beam (wavelength 780 nm, maximal power 4.5 mW, CPS 192, Thorlabs) was transformed with a telescope consisting of two identical lenses (f = 30 mm) and then focused on the cantilever. The deflections were measured with quadrant photodiode (QPD) which is sensitive to the beam position within its surface. The output signals were then improved in lock-in-amplifier (SR530, Stanford Research Systems) by increasing the signal-to-noise ratio together with the reference input of which was connected to the function generator driving the cantilevers. Then the signals were digitized in data acquisition board (PCIe-6363, National Instruments) and data was collected using Matlab.

In a typical experiment, driving frequency of function generator was adjusted over a range of approximately 10 kHz that contains the cantilever resonant frequency in the middle. Within the frequency range, 400 data points were recorded. The amplitude of the driving sinusoidal signal was set to 0.5-0.7 V peak to peak. The procedure followed in frequency response measurements was as follows. First the sample chamber was filled with desired pure fluid to the maximal working pressure between 24-27 MPa with the syringe pump. Mixtures were then obtained by transferring the second pure fluid to the sample chamber at a desired amount calculated via mass measurement. Subsequently, sample chamber was brought to desired temperature using the heating circulator. Optical measurements were performed when the equilibrium temperature and pressure are reached, typically 1-2 hours after setting of the heating circulator. The optical measurements were first performed at highest fluid pressure. Fluid pressure was then gradually decreased for consecutive optical measurements while temperature was kept constant at all times. At each pressure, resonance frequency and Q-factor was recorded for the specific cantilever with length of interest. 3 measurements were performed for the same cantilever to quantify the reproducibility.

RESULTS

The frequency response of microcantilevers in liquid, gas and supercritical fluids and fluid mixtures were investigated. Resonance frequencies and quality factors as components of frequency response were measured for supercritical CO_2, supercritical N_2 and supercritical mixtures of CO_2 and N_2 at 35 °C with 200 µm cantilevers from atmospheric pressure to 3600 psia (25MPa) (Figure 2 and 3). The frequencies and quality factors were found to decrease with increasing pressure. Decrease in resonance frequency can be explained by increase in added mass due to increase in density with pressure. Moreover, increase in viscosity with pressure results in higher viscous drag and thus lowering of Q-factor. However, decrease in the resonance frequency and quality factor curves was not identical for different compositions of $CO_2 - N_2$ mixture. A more substantial change occurred in resonance frequency and quality factor for CO_2 since the operating temperature, 35 °C, is close to the critical temperature of CO_2. The highest slope is observed at the pressures close to the critical pressure of CO_2 where phase transition occurs. In the proximity of phase transition point, change in pressure results a dramatic change in the density and viscosity thus a dramatic change in resonance frequency and quality factor. As nitrogen composition increased in the $CO_2 - N_2$ mixture, slope for both curves decreases since studied temperature and pressure was much higher than critical temperature and pressure of nitrogen.

Experimental data was analyzed using Sader's model which describes the behavior of the cantilever oscillations under the influence of hydrodynamic forces. Maali's analytical approximation to hydrodynamic function was incorporated to the model equation [2, 3, 4]. The two equations used in the model were as follows.

$$\omega_{fluid} = \omega_{vac} * [\,1 + \frac{\pi \rho W}{4 \rho_c t} * \left(1.0553 + 3.7997\sqrt{\frac{2\eta}{\rho \omega_{fluid} w^2}}\right)\,]^{-1/2} \tag{1}$$

$$Q = \frac{\frac{4\rho_c t}{\pi \rho w} + (1.0553 + 3.7997\sqrt{\frac{2\eta}{\rho \omega_{fluid} w^2})}}{3.8018\sqrt{\frac{2\eta}{\rho \omega_{fluid} w^2}} + 2.7364\frac{2\eta}{\rho \omega_{fluid} w^2}} \tag{2}$$

where w is width of cantilever (20 µm), ρ_c is cantilever density, t is thickness, η is fluid viscosity, ρ is fluid density, ω_{fluid} is angular resonance frequency, and Q is quality factor.

Density and viscosity values for pure CO_2 and pure N_2 were determined from NIST Chemistry webbook [7]. The density of a given N_2-CO_2 mixture was predicted from Gerg equation of state which gives accurate values for wide range of temperatures (from 90 to 450 K) and pressures (up to 35 MPa) involving the gas, liquid and supercritical region for mixtures [8]. Viscosity of the N_2-CO_2 mixture was calculated using Chung Equation which is commonly used for both polar and nonpolar dense gas mixtures [9]. Resonance frequency and Q-factor values were taken from measurements. The comparison of experimental data with the model was shown in Figures 2 and 3 for pure CO_2, pure N_2, and two different compositions of N_2-CO_2 mixture. A good agreement was clearly observed between the model and measurements. This indicates that, once the parameters ($\rho_c * t$ and ω_{vac}) are determined for a given microcantilever, the Sader's model can be used for measuring the density and viscosity of fluid mixtures using resonance frequency and quality factor data at a given pressure and temperature. Such measurements can be performed for mixtures at a wide range of thermodynamic states involving supercritical and near critical regions.

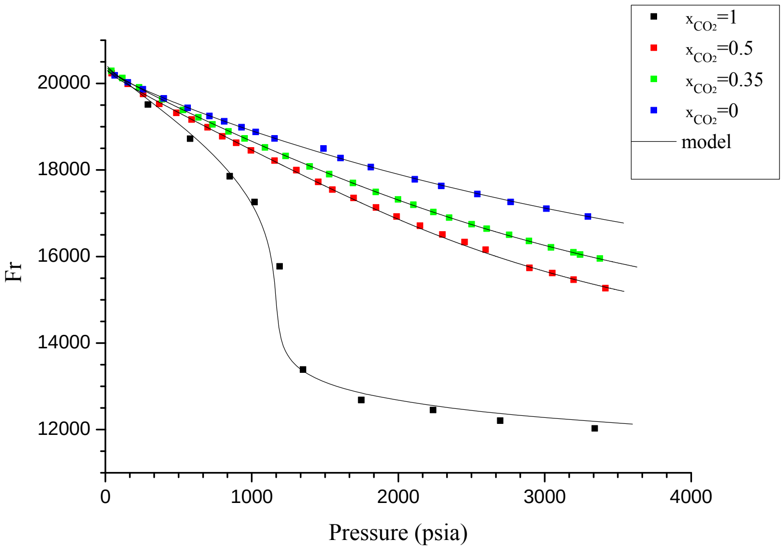

Figure 2: Variation of resonance frequency at different pressures with fitted model for 200 μm microcantilever for N_2-CO_2 binary mixture.

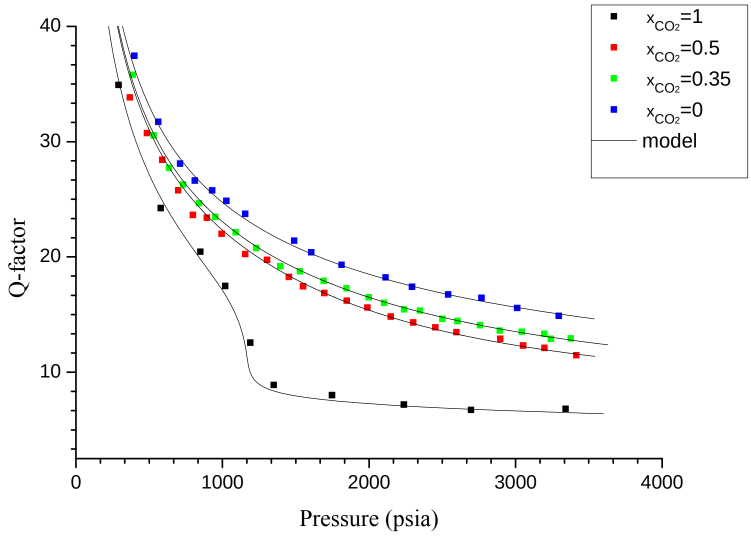

Figure 3: Variation of Q-factor at different pressures with fitted model for 200 μm microcantilever for N_2-CO_2 binary mixture.

CONCLUSION

Frequency response measurements of microcantilevers were performed for a wide range of pressures for supercritical CO_2, supercritical N_2 and supercritical mixtures of CO_2 and N_2. The experimental data was analyzed using Sader's model which characterizes the oscillatory behavior of cantilever beam in viscous fluids. A very good agreement was shown between the experimental data and the model, thus illustrating suitability of the experimental approach for density and viscosity measurements in various supercritical fluids and fluid mixtures including measurements in the mixture critical region.

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