Determination of viscosity and density of fluids using frequency response of microcantilevers

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ABSTRACT

We report on the simultaneous measurement of density and viscosity of nitrogen in gas and supercritical phases at 308.15 K and pressures up to 24 MPa. The density and viscosity were extracted from the measured frequency responses of an oscillated microcantilever immersed in N_2. To this end, a model of oscillatory motion of immersed cantilevers incorporating the effects of hydrodynamic forces was employed. Using argon as a reference fluid of known density and viscosity, cantilever calibration parameters were obtained from nonlinear regression of cantilever resonant frequencies and quality factors recorded in argon. Subsequently, these calibration parameters were used in the model equations to determine the density and viscosity of nitrogen at the given experimental pressure and temperature. In the studied pressure range, the root-mean-square deviations of the measured density and viscosity of nitrogen from the reference values obtained from NIST database were 2.5% and 5.2%, respectively.

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1. Introduction

Knowledge of density and viscosity of pure fluids and fluid mixtures at high pressures is important not only for the development of supercritical fluid-based technological processes but also for understanding the nature of intermolecular interactions at supercritical conditions. Even though there are many experimental techniques available to measure separately the density and viscosity of fluids with a high precision over a wide range of fluid pressures and temperatures [1,2], there is a growing interest to develop new techniques for simultaneous measurement of the density and viscosity. This is partly being driven by the necessity to know the fluid density in order to extract the viscosity from the raw experimental data and working equations employed in nearly all viscometers. Moreover, almost all of the thermodynamic correlations developed for the prediction of viscosity of a particular fluid contain density. Parallel measurements of fluid density

and viscosity were carried out using, for example, a rotating-body viscometer [3] or a vibrating-wire viscometer [4] combined with an independent vibrating-tube densitometer. However, the use of two separate instruments can introduce error into the measured values caused by the difficulty to maintain exactly identical experimental conditions (i.e. the fluid pressure and temperature) in both instruments. In addition, independent measurements increase required measurement time and volume of the fluid. To address these issues, Padua and co-workers carried out simultaneous viscosity and density measurements with a vibrating-wire viscometer modified by attaching a suspended buoyant body (a sinker) directly to the vibrating wire [5,6]. The presence of the sinker changed the wire tension in a density-dependent way, resulting in measurable shifts of the wire resonant frequency. A vibrating-wire viscometer in combination with a single-sinker densitometer was adopted by Seibt et al. to measure the viscosity and density of helium and nitrogen over a wide range of temperatures and pressures [7]. Krall and Sengers employed a disk suspended from a torsion wire oscillating in the studied fluid to determine the fluid density and viscosity from the measured period and amplitude damping factor of the disk oscillations [8]. However, coupling between the disk oscillation

period and damping factor in the working equations describing the system reduced the precision of the measurement for certain ranges of viscosity-to-density ratios. Evers et al. used magnetic coupling to suspend a cylindrical sinker in a fluid and transfer the buoyant forces acting on it to an external microbalance to determine the fluid density [9]. At the same time, fluid viscosity was extracted from the rate of decay of the rotational velocity of the sinker. In general, combined viscometers/densitometers based on vibrating or rotating macroscopic probes (wires, cylinders, or balls) are quite complex to construct and operate and require large sample volumes.

Oscillating microcantilevers have shown a great potential for applications as devices for the simultaneous measurement of fluid density and viscosity, providing a high sensitivity, fast response, simple and compact structure, and low sample requirements down to microliter and even nanoliter range [10,11]. Frequency response of an oscillating cantilever can be characterized by its resonant frequency, ω_R, and the quality factor of the oscillations, Q-factor [11]. ω_R is defined as the angular frequency at which the maximum amplitude of driven cantilever oscillations is observed. Q-factor is determined by the spectral bandwidth of the cantilever frequency response and it quantifies energy dissipation during oscillation. Due to its definite density and viscosity, the fluid exerts hydrodynamic forces which affect the oscillations of immersed cantilevers. These fluid forces arise from the combination of an effective added mass due to the density of the fluid moving along with the cantilever (inertial forces) and energy dissipation due to viscous drag in the fluid (friction forces). Consequently, the frequency response of a cantilever beam is strongly dependent on the properties of the fluid in which the cantilever is immersed and, thus, it can be in principle related to the density and viscosity of the fluid.

There are a number of experimental and theoretical studies that relate the density and viscosity of fluids to the frequency response of immersed microcantilevers, using hydrodynamic models of cantilever motion of various degrees of complexity. The most rigorous approach to the problem proposed by Sader is based on the solution of the equation of motion of a clamped elastic beam subject to hydrodynamic forces of the surrounding fluid [12]. The complete solution developed by Sader was subsequently simplified by Maali et al. who derived an analytical approximation to the transcendental hydrodynamic function of Sader, resulting in Eqs. (1) and (2) for the dissipation-free cantilever angular resonant frequency ω_{fluid} and quality factor Q [13]:

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

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

where ρ is the fluid density, μ is the fluid viscosity, w is the width of the cantilever, ρ_c is the cantilever density, t is the cantilever thickness, ω_{vac} is the vacuum angular resonant frequency, and the dissipation-free cantilever angular resonant frequency ω_{fluid} is related to the actual angular resonant frequency of the damped cantilever in the fluid ω_R (i.e. the angular frequency of the maximal measured amplitude of the cantilever oscillations) by

$$\omega_{\text{fluid}} = \frac{\omega_R}{\sqrt{1 - 1/2Q^2}} \tag{3}$$

Eq. (1) was used by Toda et al. to investigate the frequency response of cantilevers immersed in carbon dioxide in the vicinity of the critical point [14]. Youssry et al. used Maali's approximations to obtain formulas for the fluid density and viscosity from

the measured resonant frequency and Q-factor [15]. Boskovic et al. [16] described a method for determining the density and viscosity of an unknown fluid by calibrating the cantilevers with a reference fluid. McLoughlin et al. [17] used this method to determine the density and viscosity of a fluid mixture at ambient pressure and room temperature using reference measurements in air and two additional fluids with known properties. Shih et al. measured the density and viscosity of glycerol–water mixtures at different concentrations with a piezoelectric cantilever [18]. All of these studies on measurements of fluid density and viscosity using microcantilevers were performed at atmospheric pressure and studies in high-pressure regions are largely missing in the literature.

In our recent study [19], we addressed this challenge and developed an experimental set-up and protocols for measuring frequency response of cantilevers immersed in high-pressure fluids. Frequency response of microcantilevers immersed in gas, liquid and supercritical phases of CO_2 in the temperature range 298–323 K and pressures up to 27 MPa were successfully measured and compared to the predictions derived from Maali's approximation to Sader's model of immersed cantilever motion [19]. We observed a very good agreement between the experimentally obtained resonant frequencies and quality factors and the predictions of Sader's model, indicating that upon proper calibration, it might be possible to measure simultaneously the fluid density and viscosity at high pressures.

In this study, we report on the measurement and analysis of microcantilever frequency responses in nitrogen (N_2) and argon (Ar) in gas and supercritical phases at the temperature of 308.15 K and pressures up to 24 MPa. Using Ar as a reference fluid of precisely known density and viscosity, we calibrate the characteristic material and geometric parameters of the cantilever sensor. Subsequently, we use these calibration parameters to determine the viscosity and density of N_2 at varying pressures from the frequency responses of the cantilever immersed in this fluid and observe a good agreement between the measured values and reference data obtained from the NIST database [20].

2. Materials and methods

2.1. Materials

N_2 and Ar were supplied by Aligaz Messer with purities of 99.9% and 99.5%, respectively and were used as received.

2.2. Experimental procedure

The design and fabrication of ferromagnetic microcantilevers made of nickel were explained in detail in our previous study [19]. Cantilever used in this study had a length of approximately 200 μm, a width of approximately 20 μm, and a thickness about 1 μm. It was composed of a chromium layer with a thickness of 10–20 nm, a gold layer of 100–200 nm, and a nickel layer of 0.85–0.95 μm. The schematic representation of the cantilever together with a micrograph of the actual device is shown in Fig. 1.

As described in Ref. [19], a die with microcantilevers was mounted in a Teflon housing with an electromagnetic actuator–a coil made from Cu wire–and placed in a 50 mL cylindrical high-pressure vessel (TharSFC 05424-4). Two sapphire windows at each face of the vessel enabled monitoring the cantilevers during the experiment and recording their vibrational response using laser beam deflection (see below for details). The electrical connection for the actuation of microcantilevers in the pressure vessel was sealed using insulated CONAX Technologies TG24 T gland assemblies. Temperature of the studied fluid was controlled by circulating water through plastic tubing wrapped around the vessel using a heating circulator (Polyscience) and it was monitored with a

Fig. 1. (left) Schematic representation of microcantilever used for the fluid density and viscosity measurements (right) micrograph of the microcantilever.

T-type thermocouple (Omega) with ± 1 K accuracy. Pressure of the fluid was monitored with a pressure transducer (Omega PX 4100) with ± 0.1 MPa accuracy.

Prior to the measurements with each fluid, the connecting lines and the vessel were flushed for several times with the fluid of interest. The vessel was then filled with the fluid to the maximal desired pressure by using a TELEDYNE ISCO D Series syringe pump. In order to drive the cantilevers, a sinusoidal signal was generated by a function generator (Agilent 33220A), amplified 50 times by a high-voltage, high-frequency amplifier (Falco Systems WMA-300), and subsequently sent to the coil. Varying magnetic field generated by the coil then actuated the ferromagnetic cantilevers. 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 surface with an objective; this laser beam served to record the oscillations of the cantilever. The direction of the beam reflected from the oscillating cantilever was monitored with a quadrant photo-diode (QPD) which is sensitive to the beam position within its surface. The angle of the beam reflected from the cantilever changes due to the deflection of the cantilever and, consequently, the position of the beam on the QPD changes which results in cantilever deflection signal. The signal-to-noise ratio of the QPD deflection signal was improved by feeding the signal into a lock-in-amplifier (SR530, Stanford Research Systems) together with the reference input which was connected to the function generator driving the cantilevers. Both amplitude of the deflection and its phase shift with regard to the driving were detected by the lock-in amplifier and digitized using a data acquisition board (PCIe-6363, National Instruments) controlled from Matlab programming environment.

In a typical experiment, driving frequency of the function generator was adjusted over a range of approximately 9 kHz centered on the cantilever resonant frequency. Within this frequency range, 400 evenly spaced data points were recorded. The amplitude of the driving sinusoidal signal was set to 3 V peak to peak before 50 times amplification. In the beginning of a series of measurements, the sample chamber was filled with desired fluid to a pressure between 24–25 MPa with the syringe pump. Subsequently, the sample chamber was brought to the desired temperature using the heating circulator. Measurements of the cantilever frequency response were performed when the temperature and pressure became stable, typically 1–2 h after setting of the heating circulator. The cantilever frequency response measurements were first performed at the highest fluid pressure. Fluid pressure was then gradually decreased for consecutive measurements in the series while the temperature was kept constant at all times. At each pressure, the dissipation-free cantilever resonant frequency ω_{fluid} and the quality factor Q were determined by fitting the fundamental measured resonance peak to Eq. (4) which approximates the oscillation of an elastic cantilever beam by a simple damped harmonic oscillator in the limit of small dissipation [12]:

$$A(\omega) = \frac{A_0 \omega_{fluid}^2}{\sqrt{\left(\omega^2 - \omega_{fluid}^2\right)^2 + \omega^2 \omega_{fluid}^2 / Q^2}} \qquad (4)$$

where A_0 is the zero-frequency amplitude of the response and ω is the angular driving frequency. For each pressure, three successive measurements were performed and the reported values are the average of the three values at the given fluid pressure and temperature. The mean value of the relative standard deviation of resonant frequency and Q-factor measurements was 0.1% and 3.6%, respectively, while the maximum deviations were 0.3% and 9.6%, respectively.

3. Results and discussion

The dissipation-free resonant frequency, $f_{fluid} = \omega_{fluid}/2\pi$, and Q-factor measured with a 200 μm cantilever immersed in N_2 and Ar at 308.15 K and pressures up to 24 MPa are given in Figs. 2 and 3. The decrease in the resonant frequency observed with increasing
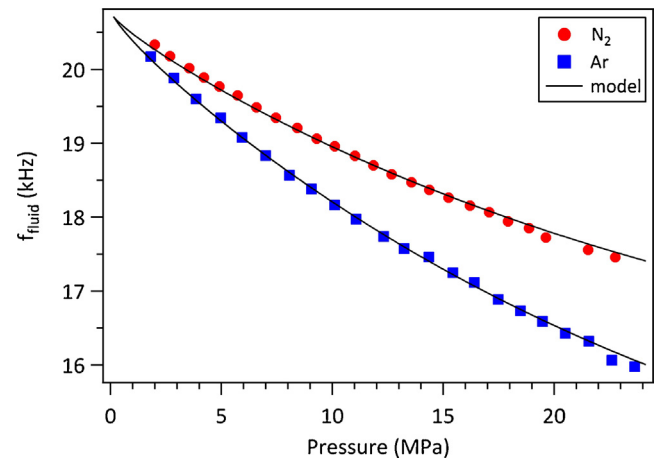

Fig. 2. Resonant frequency f_{fluid} of a driven microcantilever determined in N_2 and Ar at 308.15 K. Symbols: experimental data points, solid lines: fit of experimental data to Eq. (1).

Fig. 3. Q-factor of a driven microcantilever determined in N_2 and Ar at 308.15 K. Symbols: experimental data points, solid lines: fit of experimental data to Eq. (2).
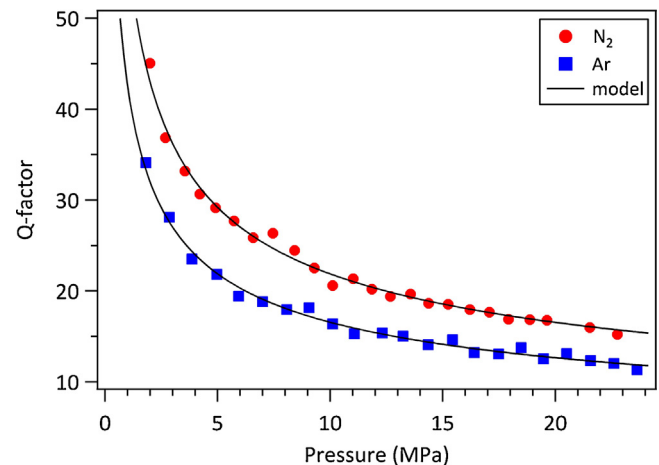
Table 1
Fitted calibration parameters for the studied cantilever.

Fitted parameters	N_2	Ar	Relative difference between N_2 and Ar parameter values $100 \times (N_2 - Ar)/N_2$ [%]
$\rho_c \times t$ (kg/m^2)	0.0111	0.0109	1.8
ω_{vac} (rad/s)	130,627.4	130,841.1	0.2
w (μm)	18.8	19.0	1.0

fluid pressure can be attributed to the increase in the fluid mass moving along with the cantilever due to an increase in the fluid density with the pressure. Moreover, the effective volume of the fluid that is affected by cantilever oscillations increases with the fluid viscosity; thus, the increase of viscosity with increasing pressure contributes further to the decrease of the cantilever resonant frequency. Increase in viscosity also causes an increase in viscous damping and energy dissipation which translates into a decrease in the Q-factor value as pressure increases. The resonant frequency changes smoothly with pressure within the studied pressure range, including the phase transition pressures where a transition from

was measured with optical microscopy as 19.6 μm. From the cantilever frequency response recorded in evacuated high-pressure vessel (residual pressure 7 T), the vacuum resonant frequency (f_{vac}) was determined to be 20,708 Hz. Cantilever density × thickness was calculated as 0.011 kg/m^2 by multiplying the average density of the cantilever by the total thickness of the cantilever. The average density of the cantilever was calculated using:

$$\rho_c = \frac{\sum_{i=1}^{3} V_i \rho_i}{\sum_{i=1}^{3} V_i} \tag{6}$$

where ρ_i and V_i is the density and volume of each layer of the microcantilever (Ni: density 8900 kg/m^3, thickness 1000 nm; Au: density 19,300 kg/m^3, thickness 110 nm; Cr: density 7200 kg/m^3, thickness 15 nm).

These values are close to the values regressed from the experimental data and show that Sader's model captures very well the physics of the immersed cantilever oscillations.

This result suggests that it should be possible to use the cantilever frequency response to measure simultaneously the density and viscosity of the fluid. To that end, Eqs. (1) and (2) can be re-written in the following form:

$$\omega_{fluid,exp} - \omega_{vac}\left[1 + \frac{\pi \rho w}{4\rho_c t} \times \left(1.0553 + 3.7997\sqrt{\frac{2\mu}{\rho \omega_{fluid,exp} w^2}}\right)\right]^{-1/2} = 0 \tag{7}$$

$$Q_{exp} - \frac{\frac{4\rho_c t}{\pi \rho w} + \left(1.0553 + 3.7997\sqrt{2\mu/\rho \omega_{fluid,exp} w^2}\right)}{3.8018\sqrt{2\mu/\rho \omega_{fluid,exp} w^2} + 2.7364\left(2\mu/\rho \omega_{fluid,exp} w^2\right)} = 0 \tag{8}$$

supercritical to gaseous phase occurs (P_c = 3.396 MPa for N_2 and P_c = 4.863 MPa for Ar). This behavior is a result of smooth changes of the fluid density and viscosity with fluid pressure for operating temperature well above the fluid critical point (T_C = 126.2 K for N_2 and T_C = 150.7 K for Ar). Q-factor for both fluids follows a similar behavior, a uniform decrease with pressure. The rate of the decrease in Q-factor is more pronounced at lower pressures.

In order to test the validity of Maali's approximation to Sader's hydrodynamic model of the immersed cantilever motion [13], experimental values of the cantilever angular resonant frequency, $\omega_{fluid,exp,i}$ and Q-factor, $Q_{exp,i}$ were fitted to model Eqs. (1) and (2) by minimizing the objective function F given by

At a certain fluid temperature and pressure, the cantilever angular resonant frequency $\omega_{fluid,exp}$ and quality factor Q_{exp} are measured and inserted into Eqs. (7) and (8) together with the three cantilever calibration parameters ($\rho_c \times t$, ω_{vac}, w). Subsequently, the density and viscosity of the studied fluid satisfying simultaneously Eqs. (7) and (8) can be found using an appropriate numerical method.

As described above, cantilever calibration parameters can be in principle determined independently using different instruments. However, due to the variations in the cantilever manufacturing process, this characterization must be generally done for each individual cantilever, which is neither easy nor convenient. Moreover,

$$F = \sum_i \left\{ \left(\omega_{fluid,exp,i} - \omega_{vac}\left[1 + \frac{\pi \rho w}{4\rho_c t}\left(1.0553 + 3.7997\sqrt{\frac{2\mu}{\rho \omega_{fluid,exp,i} w^2}}\right)\right]^{-1/2}\right)^2 + \right.$$
$$\left. \left(Q_{exp,i} - \frac{\frac{4\rho_c t}{\pi \rho w} + \left(1.0553 + 3.7997\sqrt{2\mu/\rho \omega_{fluid,exp,i} w^2}\right)}{3.8018\sqrt{2\mu/\rho \omega_{fluid,exp,i} w^2} + 2.7364\left(2\mu/\rho \omega_{fluid,exp,i} w^2\right)}\right)^2\right\} \tag{5}$$

where the summation index i runs over all experimental values obtained at all pressures at a particular temperature.

The three parameters which were the vacuum resonant frequency (ω_{vac}), cantilever density × thickness ($\rho_c \times t$), and cantilever width (w) were regressed from the experimental data. To this end, density and viscosity values for both fluids required for the fitting were obtained from NIST Chemistry webbook [20]. As shown in Figs. 2 and 3, a very good agreement between the model and the experimental data was observed for both studied fluids. The fitted parameters ($\rho_c \times t$, ω_{vac}, w) summarized in Table 1 are very similar for both fluids. This is expected since the cantilever properties should be independent of the type of fluid. An independent verification of the values of the fitted parameters was obtained from direct experiments and calculations. The width of the cantilever

cantilever dimensions and elastic modulus change with temperature [19]. In order to estimate the influence of errors in the cantilever calibration parameters on the measured values of fluid density and viscosity, we calculated the deviations in the measured density and viscosity of Ar due to the deviations in these three parameters ($\rho_c \times t$, ω_{vac}, w) from their true values. A 1% deviation in an individual calibration parameter was introduced (keeping the other two parameters constant) and then the change in the density and viscosity of Ar was calculated. The results of these calculations are summarized in Figs. 4 and 5. While the density and viscosity are fairly insensitive to deviations in $\rho_c \times t$ and w, a 1% error in ω_{vac} leads to large systematic deviations in the calculated values of
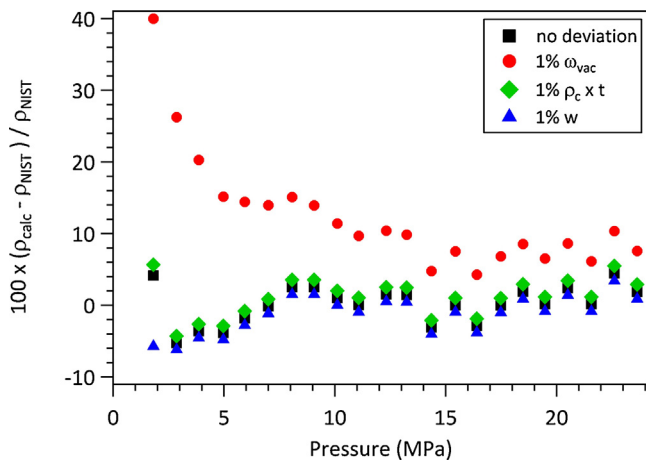
Fig. 4. The effect of errors in the cantilever calibration parameters on the relative error of density of Ar at 308.15 K.
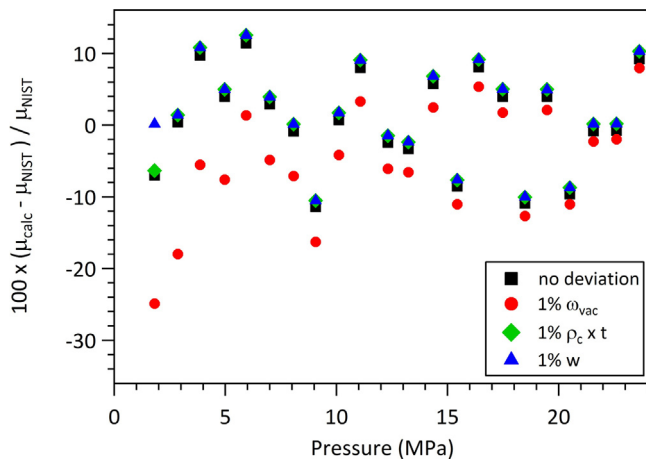

Fig. 6. Relative deviation of the measured density of N_2 from the expected values. Experimental values of N_2 density were calculated using Ar as the reference fluid.

Fig. 5. The effect of errors in the cantilever calibration parameters on the relative error of viscosity of Ar at 308.15 K.

Fig. 7. Relative deviation of the measured viscosity of N_2 from the expected values. Experimental values of N_2 viscosity were calculated using Ar as the reference fluid.

density and viscosity (ρ_{calc}, μ_{calc}) with respect to the expected values (ρ_{NIST}, μ_{NIST}) determined from the NIST reference data [20].

As an alternative to the direct measurement or calculation, cantilever calibration parameters can be determined from a series of frequency-response measurements in a reference fluid with density and viscosity known very accurately for each individual measurement in the series. This way, one does not need to know the exact details about the composition, geometry or any mechanical properties of the cantilever, since this information can be obtained from experimental data by regression. We adopted this approach with Ar as the reference fluid and determined the density and viscosity of N_2 using the cantilever calibration parameters regressed from the frequency response data of Ar. The deviations of the calculated density and viscosity of N_2 (ρ_{calc}, μ_{calc}) from the values (ρ_{NIST}, μ_{NIST}) obtained from the NIST database are presented in Figs. 6 and 7. As illustrated by these figures, no systematic deviation of the measured and expected values is observed for both density and viscosity and their error is randomly scattered about the zero value. The root-mean-square deviation of density and viscosity were 2.5% and 5.2% in the studied pressure range while the maximum deviations were below 4.9% and 11.4%, respectively.

These results are very promising and show the potential of the technique for accurate, simultaneous measurements of the fluid viscosity and density. From the comparison of Figs. 6 and 7, it follows that density could be measured with a higher precision compared to viscosity. One possible reason is that the resonant
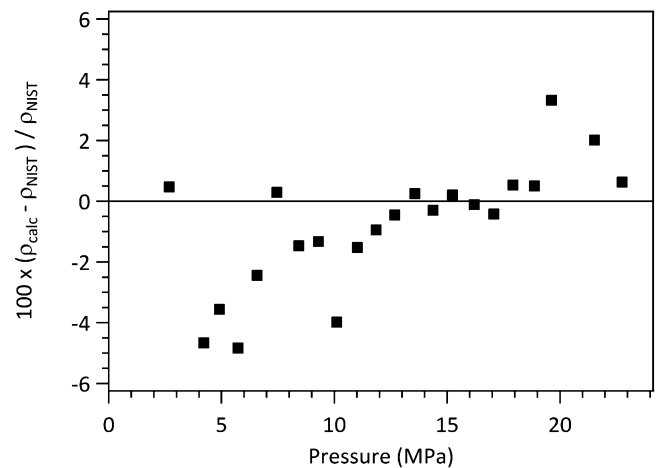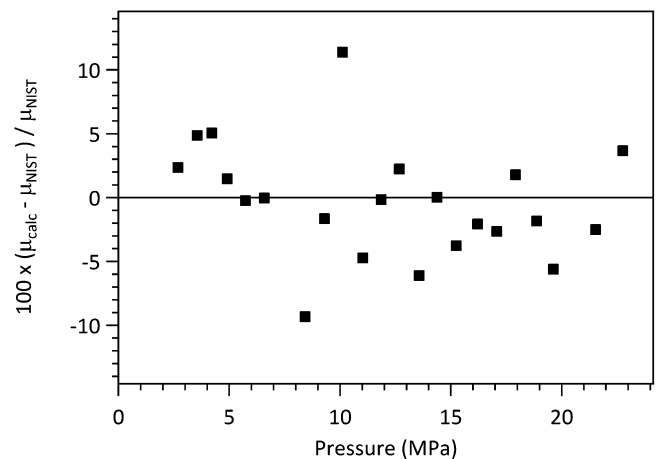
frequency can be determined more precisely from the measured frequency responses than the Q-factor. Relative standard deviation of the measured resonant frequency given by (standard deviation/average × 100) was lower than that of the Q-factor for the measurements with both fluids at the studied pressure range. In particular, the average relative standard deviations of the resonant frequency and the Q-factor in all N_2 and Ar experiments were 0.1% and 3.6%, respectively. Inspection of Eqs. (1) and (2) reveals that the resonant frequency ω_{fluid} depends only weakly on the fluid viscosity ($\omega_{fluid} \propto \mu^{-1/4}$) whereas the dependence of the Q-factor on viscosity is much stronger (leading term of $Q \propto \mu^{-1/2}$). Thus, in solving coupled Eqs. (7) and (8) for the fluid density and viscosity, contribution of experimental values of the Q-factor to the calculated viscosity is more important than the contribution of measured resonant frequencies. Higher error in the measured Q-factor values then results in less precise viscosity values. On the other hand, leading terms of both ω_{fluid} and Q depend on the fluid density as $\propto \rho^{-1/2}$. Consequently, measured values of ω_{fluid} and Q contribute approximately equally to the measured density values and the effect of random error caused by high variations of the Q-factor is somewhat reduced by more precise measurements of ω_{fluid}.

In general, it is possible that the fluid molecules might adsorb on the surface of the cantilever which would affect the resonant frequency and the Q-factor because of an increase in the mass of the cantilever due to the mass of the adsorbed molecules. This effect is

not accounted for in Sader's model and, thus, it does not enter into the equations used to extract density and viscosity. Moreover, the effect of adsorption would not be constant in the pressure range investigated since the amount of adsorbed fluid molecules would increase with increasing pressure. In order to quantify the errors caused by this effect, we calculated the maximum amount of fluid that can be adsorbed on the surface of the cantilever assuming that the fluid molecules cover the surface as a tightly packed monolayer. For a cantilever with the total surface area of $8 \times 10^{-9}\,\mathrm{m}^2$, the maximum amount of N_2 that can be adsorbed is $2.3 \times 10^{-12}\,\mathrm{g}$. We inserted the density and viscosity data of N_2 to Eqs. (7) and (8), together with the vacuum resonant frequency and the cantilever width, and used the two different values of $\rho_c \times t$ determined by including and excluding monolayer fluid adsorption, respectively. Subsequently, we calculated the resonant frequency and the Q-factor in order to relate the change in the cantilever mass to the changes in ω_{fluid} and Q. The calculation was performed for N_2 at the highest pressure where ω_{fluid} and Q were the lowest. Resulting changes in ω_{fluid} and Q were found to be 0.01% and 0.04% which is much lower than the standard deviations in our measurements. Hence, we can conclude that the fluid adsorption has negligible effect on the determination of the fluid density and viscosity using the cantilever frequency response.

The high-pressure vessel used in our experiments imposes limitations on the accessible ranges of the fluid temperature and pressure (maximum temperature 150 °C (423 K) and maximum pressure 6000 psi (41 MPa), as specified by the manufacturer). These operating conditions can be further extended by using different high-pressure vessel designs [21]. When working within an extended range of fluid temperatures, stability of the microcantilever sensor calibration becomes an issue. As discussed by Uzunlar et al. [19], change in temperature ΔT affects the dimensions and elastic modulus of the cantilevers and, thus, calibration parameters ($\rho_c \times t$, ω_{vac}, w) also change. Cantilever linear dimensions (t,w) are proportional to $\sim(1 + \alpha \Delta T)$ which implies that the cantilever density ρ_c decreases with temperature as $\sim(1 + \alpha \Delta T)^{-3}$ where α is the coefficient of thermal expansion of the cantilever material. Similarly, elastic modulus of the cantilever changes as $\sim(1 + \beta \Delta T)$ where β is the coefficient of thermal dependence of the elastic modulus. Consequently, the vacuum resonant frequency ω_{vac} scales with temperature as $\sim(1 + \alpha \Delta T)^{0.5}(1 + \beta \Delta T)^{0.5}$. The magnitude of the temperature-induced changes of cantilever calibration parameters is given by the values of coefficients α and β and depends on the material of the cantilever. In order to avoid systematic errors in the measured values of density and viscosity, one-time calibration of the cantilever sensor with a reference fluid should be carried out at different temperatures within the range of interest. Subsequently, the calibration parameters for a particular experimental temperature can be determined by interpolation.

In the present study, experiments with N_2 and Ar at 308.15 K and pressures up to 24 MPa were carried out. This translates into the range of the fluid density and viscosity of 2–380 kg/m^3 and 18–33 µPa s, respectively. However, the maximum values of density and viscosity (380 kg/m^3 and 33 µPa s, respectively) obtained do not represent the upper limits of microcantilever-based measurements. In our previous study [19], cantilever frequency responses were recorded in carbon dioxide at densities up to 900 kg/m^3 and viscosities up to 90 µPa s. A very good agreement between the experimental data and model Eqs. (1) and (2) was observed, indicating that such density and viscosity values can be reliably measured. Moreover, there are several studies using microcantilevers that measured fluid viscosities in mPa s range at atmospheric pressures. For example, Braun and coworkers developed an experimental setup where the cantilever frequency response was measured using optical deflection and they validated the accuracy of their system in the viscosity range of 1–20 mPa s

[22]. It is reasonable to believe that these atmospheric-pressure measurements can be replicated also at high fluid pressures associated with the supercritical fluid region.

4. Conclusion

We have determined simultaneously the density and viscosity of N_2 at 308.15 K and pressures up to 24 MPa, using the frequency response of an externally driven microcantilever immersed in the fluid. Resonant frequencies and quality factors of the vibrating cantilever were measured at varying fluid pressures and analyzed using the model of immersed cantilever oscillations under the influence of hydrodynamic forces. In the first step, the theoretical model of cantilever oscillations was employed to determine the cantilever calibration parameters from a series of measurements carried out in a reference fluid (Ar) with accurately known density and viscosity. Subsequently, the density and viscosity of N_2 were determined by using the calibration parameters in the model equations, together with the resonant frequencies and Q-factors recorded in N_2. Using this procedure, we have obtained the density and viscosity of nitrogen with root-mean-square relative deviations of 2.5% and 5.2%, respectively, at the studied pressure range, while the maximum measurement errors were below 4.9% and 11.4%, respectively. Thus, microcantilever-based sensors can offer a good measurement precision combined with a simple experimental design and straightforward operation.

Our study represents the first systematic measurement of density and viscosity of supercritical fluids in a wide pressure range using the frequency response of microcantilevers. Even though we made measurements with pure fluids, our technique can be extended to supercritical mixtures or complex systems such as polymer–SCF mixtures. Preliminary studies of supercritical N_2–CO_2 mixtures have been already performed; their analysis will be the subject of a future manuscript. Since the measurements with cantilevers require very small sample volumes, compact and portable microcantilever-based sensors might enable continuous monitoring of chemical reactions in a fluid or physicochemical processes such as gelation or solidification in microfluidic applications at high temperatures and pressures by observing changes in density and viscosity. The cantilevers can also be used as high-pressure sensors in microreactor systems for samples with constant density or composition. Since the cantilever motion in the fluid is affected only by the fluid properties in the immediate vicinity of the cantilever, our experimental technique can be also applied to make localized measurements in binary phase (liquid–gas), tertiary phase (liquid–liquid–gas), or inhomogeneous systems.

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