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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.

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

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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]:

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

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

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

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

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