Viscosity and Density Measurements of Compressed Liquids

J P Martin Trusler

Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.

1. Introduction

In our laboratory, we use a vibrating-wire apparatus that provides for simultaneous determination of viscosity and density for liquids over wide ranges of temperature and pressure. The working equations of this instrument are well established and are summarised below. This report also contains a full description of the apparatus and experimental methods employed.

2. Working Equations of the Vibrating-Wire Instrument

Our implementation [1] of the steady-state vibrating-wire technique is similar to that described by Audonnet and Pádua [2] in which the wire is driven at frequency \( f \) by a constant sinusoidal current \( I \), and the emf \( V(f) \) generated across the vibrating wire is measured with a two-phase lock-in amplifier. This measured emf generally comprises two terms: the first, \( V_1(f) \), arises from the electrical impedance of the stationary wire; while the second, \( V_2(f) \), arises from the motion of the wire. In the analysis, we express the complex function \( V_1 \) as

\[
V_1(f) = a + ib + icf,
\]

where \( a, b, \) and \( c \) are real constants. The second contribution is given by [3,4]

\[
V_2 = \frac{\Lambda f}{f_0^2 - f^2(1 + \beta) + f^2(\beta' + 2\Delta_0)i},
\]

Here, \( f_0 \) is the ‘buoyancy corrected’ fundamental transverse resonance frequency of the wire in vacuum which is related to the true vacuum resonance frequency, \( f_{0,\text{vac}} \), by

\[
f_0^2 = f_{0,\text{vac}}^2 - \frac{gV_w\rho}{16\pi\rho_sR^2L^2}.
\]

Here, \( g \) is the acceleration of gravity, \( V_w \) is the volume of the weight, \( \rho \) is the density of the fluid, \( \rho_s \) is the density of the wire, \( R \) is the radius of the wire, and \( L \) is the half length of the wire. Typically, the true vacuum resonance frequency \( f_{0,\text{vac}} \) and the internal damping term \( \Delta_0 \) are determined in calibration measurements and \( f_0 \) is calculated for the state of interest from equation (3). The other parameters in equation (2) are an amplitude \( \Lambda \), and two terms, \( \beta \) and \( \beta' \), that are related to the density \( \rho \) and viscosity \( \eta \) of the fluid by the hydrodynamic theory [3,4] as follows:
\[ \beta = (\rho / \rho_s) \{2 \cdot \Im(A) - 1\} \quad (4) \]
\[ \beta' = (\rho / \rho_s) 2 \cdot \Re(A) . \quad (5) \]

In equations (4) and (5), \( A \) is given by

\[ A = i \left[ 1 + \frac{2K_i(\sqrt{\Omega})}{(\sqrt{\Omega})K_0(\sqrt{\Omega})} \right] \quad (6) \]

where \( \Omega \) is defined by the relation

\[ \Omega = \frac{\rho 2 \pi f R^2}{\eta}. \quad (7) \]

Experimentally, one measures the real and imaginary components of \( V \) as a function of frequency \( f \) for frequencies in the neighbourhood of \( f_0 \) in the fluid of interest. Then the parameters \( a, b, c, \Lambda, \rho \) and \( \eta \) are fitted by \( V(f) = V_1(f) + V_2(f) \) making use of equations (1)-(7).

Theoretical treatments of the vibrating wire have normally considered simple end conditions such as pinned, clamped, or free ends [3]. Typically, end-pinned conditions are assumed [5] but experimental vacuum frequencies are found to deviate from the values predicted under that assumption. To reconcile this discrepancy, we write the true vacuum resonance frequency as

\[ f_{0,\text{vac}} = \frac{1}{4} \kappa \left( \frac{\pi^2 E R^2 \kappa^2}{16 \rho_s L^4} + \frac{g M_w}{\pi \rho_s R^2 L^2} \right)^{1/2} \quad (8) \]

where \( E \) is Young's modulus for the wire, \( M_w \) is the mass of the suspended weight, and \( \kappa \) is a parameter that reflects the end conditions. For end-pinned conditions, \( \kappa \) is exactly unity while, for end clamped conditions, \( \kappa \approx 1.05 \). In the present work, \( \kappa \) was adjusted to match an experimental measurement of the vacuum resonance frequency at one temperature.

3. Instrument Design

The vibrating wire viscometer was designed to operate in the viscosity range 0.3 to 30 mPa·s and at densities ranging from 600 to 1000 kg·m\(^{-3}\). As shown in Fig. 1, the vibrating wire and magnetic assembly were housed in a commercially-available pressure vessel (HIP Model R1-10-30) rated for operation at pressures up to 200 MPa. The temperature of the fluid was inferred from the reading of a platinum resistance thermometer (PRT) which was mounted in a well in the cap of the pressure vessel. This thermometer was calibrated with an uncertainty of ±0.01 K. The pressure was measured in the external pipework by means of a Paroscientific transducer (Model 40K-110) with a full scale reading of 276 MPa and an uncertainty of ±0.05 MPa.
Fig. 1. The vibrating-wire instrument.

The pressure vessel was enclosed in a massive aluminium-block thermostat and insulated from the environment with 40 mm thick Kaowool V.F. ceramic fibreboard. The temperature of the block was controlled in three zones (top 1/5th, middle 3/5ths, and lower 1/5th) by means of PID controllers (Eurotherm 2210e) operating with PRT sensors and a set of 10 cartridge heaters each rated at 110 W. This arrangement was normally able to keep the temperature stable and uniform to within ±0.05 K over a period of days. The equipment has been modified slightly from that described in [1]. The modification was the addition of a heat exchanger, attached to one face of the aluminium block, through which refrigerated liquid could be circulated in order to permit operation at temperatures below ambient. This heat exchanger was operated with the liquid feed at a temperature 2 to 3 K below the desired control point.

Several different vibrating wires have been used over a period of time. All have been taken from the same batch of gold-plated tungsten wire with a nominal radius of 50 μm. Since the radius of the wire varies along the length of a single reel, each new wire has to be calibrated before use as described below. The key parameters of the apparatus are listed in Table I where \( L, R, \Delta_0, \kappa \) and \( V \) are the values obtained with the most recent wire fitted to the apparatus.
Table 1. Cell Parameters

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<tr>
<th>Parameters</th>
<th>Value</th>
<th>Source</th>
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<tr>
<td>Volume</td>
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<tr>
<td><strong>Tungsten Wire</strong></td>
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<td>Half-Length</td>
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<td>measured</td>
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<tr>
<td>Radius</td>
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<tr>
<td>Density</td>
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<td>from supplier</td>
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<tr>
<td>Young's modulus</td>
<td>E 411 GPa</td>
<td>from supplier</td>
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<tr>
<td>Internal Damping</td>
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<td>measured</td>
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<tr>
<td>Thermal expansion</td>
<td>αₙ 4.5×10⁻⁶ K⁻¹</td>
<td>from supplier</td>
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<tr>
<td>End condition perturbation</td>
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<tr>
<td><strong>Aluminum Mass</strong></td>
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<tr>
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<tr>
<td>Thermal expansion</td>
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<td>ref. [6]</td>
</tr>
<tr>
<td>Compressibility</td>
<td>β 1.32×10⁻¹¹ Pa⁻¹</td>
<td>ref. [7]</td>
</tr>
</tbody>
</table>

The four-wire circuit shown in figure 2 was used to drive and detect motion of the vibrating wire. The sine-wave oscillator (built into the Stanford Research Systems model SRS830 lock-in amplifier) could be operated at drive voltages of between 0.004 and 5.000 V rms and the frequency could be set in increments of 0.1 Hz. In order to achieve a constant driving current, a series resistor $R_s = 1.0 \, \Omega$ was employed. This was chosen to be much larger than the resistance of the wire, which was about 0.5 Ω. Terminals A and B were connected to the differential inputs of the lock-in amplifier.

![Fig. 2. Measurement circuit](image_url)

The lock-in amplifier was operated with offset real and imaginary voltage readings so as to permit measurements to be made over the most sensitive range possible. These offsets were absorbed into the parameters $a$ and $b$.

The apparatus is illustrated in figure 3 below.
4. Calibration and Testing

Calibration of the apparatus is normally performed at $T = 298.15$ K by means of measurements in both ambient air and $n$-octane at $p = 0.1$ MPa. The true vacuum resonance frequency (giving the value of $\kappa$) and the internal damping parameter $\Delta_0$ were inferred from the measurement in ambient air. This is preferable to attempting a measurement under vacuum because the small-bore pressure tubing used made it difficult to achieve a sufficiently good vacuum in the cell. The viscosity and density of air were obtained from reference [7]. The radius of the wire and the volume of the suspended mass were obtained from the measurement in $n$-octane and the values of the density and viscosity of that liquid reported by Caudwell [8] ($\rho = 698.4$ kg·m$^{-3}$ and $\eta = 0.510$ mPa·s at $T = 298.15$ K and $p = 0.1$ MPa).

To verify proper operation of a new vibrating wire, the usual practice is to measure a small number of additional state points in the calibration fluid and to compare the results with those reported in [8]. Typically, the measured density agreed to within ±0.1% and the measured viscosity to within ±1%.

The overall measurement uncertainties are summarised as follows:
- viscosity ±2%
- density ±0.2%
- temperature ±0.02K
- pressure ±0.05 MPa

Figures 4 and 5 illustrate typical results.
6. Data Correlation

There are numerous ways in which the data might be correlated. Here we present simple correlations of both density and viscosity that take temperature and pressure as the
independent variables. This is in accord with the measurement approach and it is also the most convenient method for application.

8.1 Correlation of the density
Typically, the density may be correlated with sufficient accuracy by the modified Tait equation

\[ \rho = \rho_0 \left(1 - C \log_{10} \left( \frac{\rho + B}{\rho_0 + B} \right) \right)^{-1}, \]  

(10)

where \( \rho_0 = 0.1 \text{ MPa} \), \( \rho_0 \) is the density at \( p = p_0 \), \( C \) is a constant and \( B \) is a temperature dependent parameter. Typically, we correlated \( \rho_0 \) and \( B \) as follows:

\[ \rho_0 \text{/(kg·m}^{-3}) = \sum_{i=0}^{2} a_i (T \text{/K})^i \]  

(11)

\[ B/\text{MPa} = \sum_{i=0}^{2} b_i (T \text{/K})^i \]  

(12)

In order to establish the parameters of this correlation, equation (10) is first applied to individual ‘isotherms’ (ignoring small temperature differences) and \( \rho_0, B \) and \( C \) are adjusted by trial. Typically, it is initially assumed that \( C = 0.2 \) and that \( \rho_0 \) is equal to the measured density at the lowest pressure. The three parameters are then adjusted, first manually and then in an optimisation loop, so as to minimise the differences between the measured and correlated values.

Once rough values of \( \rho_0, B \) and \( C \) are obtained at each temperature, the parameters \( a_i \) and \( b_i \) may be estimated by linear regressions with equations (11) and (12), and a mean value of \( C \) is calculated. Finally, all seven parameters (\( a_0, a_1, a_2, b_0, b_1, b_2 \) and \( C \)) are adjusted in a simultaneous non-linear optimisation so as to minimise the absolute average deviation for an entire data set. Typically, the final absolute average deviation obtained is around 0.05%.

8.2 Correlation of the viscosity
The viscosity may usually be correlated by the equation [9]

\[ \eta = A_\eta \exp \left( \frac{B_\eta}{T - C_\eta} \right) \left( \frac{\rho + E}{\rho_0 + E} \right)^D, \]  

(13)

where \( A_\eta, B_\eta \) and \( C_\eta \) are constants, \( \rho_0 = 0.1 \text{ MPa} \) as before, and \( D \) and \( E \) are functions of temperature as follows:

\[ D = \sum_{i=0}^{1} d_i (K/T)^i \]  

(14)
\[ E \text{ / MPa} = \sum_{i=0}^{2} e_i (T / K)^i \] (15)

The correlating procedure is as follows. First, individual isotherms were fitted by the equation

\[ \eta = \eta_0 \left( \frac{p + E}{p_0 + E} \right)^d, \] (16)

to obtain \( \eta_0 \) (the viscosity at \( p = p_0 \)), \( E \) and \( D \) at each temperature. Second, we estimated \( A_\eta \), \( B_\eta \), and \( C_\eta \) by linear regression with the equation

\[ \ln \eta_0 = \ln A_\eta + \left( \frac{B_\eta}{T - C_\eta} \right), \] (17)

using various trial values of \( C_\eta \) which are adjusted manually to achieve a good fit. Next, we estimated the parameters \( d_i \) and \( e_i \) by linear regressions with equations (14) and (15). Finally, all eight parameters (\( A_\eta \), \( B_\eta \), \( C_\eta \), \( d_0 \), \( d_1 \), \( e_0 \), \( e_1 \), and \( e_2 \)) are adjusted in a simultaneous non-linear optimisation so as to minimise the absolute average deviation for an entire data set. Typically, the final absolute average deviation obtained is around 2%.

References