Gas viscosity-ratio measurements with two-capillary viscometers

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Abstract

Viscosity-ratio measurements made with capillary viscometers exploit the accurate values of the viscosity of helium calculated \textit{ab initio}. Accurate values of the argon-to-helium viscosity ratio are now used for primary acoustic gas thermometry and for acoustic redeterminations of the Boltzmann constant. Accurate viscosity ratio measurements enable the calibration of laminar flow meters with surrogate gases and their use with process gases. We review ratio viscometers that comprise one or two capillaries. A single capillary is a ratio viscometer when it is used to measure multiple gases, while a two-capillary viscometer is intended for ratio measurements. We consider only dilute gases and emphasize the two-capillary gas viscometer.
1. Introduction

In this chapter, we discuss the usefulness of gas viscosity ratios and how to obtain such ratios with single-capillary viscometers. Then, we focus on the two-capillary gas viscometer devised by May et al. [1,2] to measure gas viscosity ratios with very low uncertainties, and subsequently used by Zhang et al. [3]. Further details, including a review of four-capillary viscometers and proposals to (i) extend the two-capillary viscometer technique to high pressures, and (ii) measure the water-to-helium viscosity ratio, will be published elsewhere [4].

The Ar-to-He gas viscosity ratios measured by May et al. have proved useful for primary acoustic thermometry [5] and acoustic redeterminations of the Boltzmann constant [6]. These acoustic measurements require accurate values of the thermal conductivity of low density argon, which can be obtained by combining the measured Ar-to-He viscosity ratio with theoretical values of helium’s viscosity and the Prandtl number for argon. The measured Ar-to-He viscosity ratio also has been used in the temperature range 200 K < T < 400 K to test ab initio calculations of the viscosity and thermal conductivity of argon [7,8]. The uncertainty of the viscosity calculated from the Ar-Ar interatomic potential is estimated to be less than 0.1% at temperatures as low as 80 K [8]; however, the uncertainty from the use of classical (rather than quantum-mechanical) calculation has not been quantified [5]. Thus, low uncertainty gas viscosity-ratio measurements at temperatures below 200 K would be a useful guide to theory. Similar measurements above 400 K would help resolve the current tension between measurements and the theory for the viscosity of hydrogen [9].
The widespread practice of calibrating laminar flow meters with surrogate gases (such as helium or argon) and then using them to meter process gases requires accurate surrogate-to-process gas viscosity ratios. [10] With this application in mind, Berg and Moldover [11] reviewed two hundred viscosity measurements near the reference temperature $T_{\text{ref}} = 298.15$ K and zero density for 11 gases, and determined the viscosity ratios among the gases with an uncertainty less than 0.04 %, which is smaller than the uncertainty of the separate absolute measurements.¹ They then anchored the measured viscosity ratios to the remarkably low uncertainty

$$\eta_{0,\text{Ref}}^{\text{He}} = (19.8253 \pm 0.0002) \, \mu\text{Pa s},$$

(1)
calculated ab initio by Cencek et al [12] (using only quantum mechanics, statistical mechanics, and fundamental constants) for helium at 298 K and zero density. (In Eq. (1) and below, the the superscript is the gas $g$, the first subscript on the symbol $\eta$ is the pressure, and the second subscript is the temperature.)

Table 1 reproduces the viscosities recommended in Ref [11].

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¹ Unless otherwise stated, all uncertainties are one standard uncertainty which corresponds to a 68 % confidence interval.
Table 1. Reference viscosities, reproduced from [11], obtained by fitting 235 viscosity ratios measured using 18 instruments. The first column gives the recommended value of $\eta_{0,T_{\text{ref}}}$, the viscosity at the temperature $T_{\text{ref}} = 298.15 \, \text{K}$ and zero density, and its standard ($k = 1$) uncertainty. The value for helium was calculated in [12]. The second column gives the corresponding ratios relative to helium. The third column gives the isothermal density derivative of the viscosity that was used to adjust measurements of viscosity to zero density. The fourth column gives the exponent $a$ in the expression $\eta_{0,T}^g = \eta_{0,T_{\text{ref}}}^g (T / T_{\text{ref}})^a$ that was used to adjust $\eta_{0,T_{\text{ref}}}^g$ to $T_{\text{ref}}$. See [11] for details and references.

<table>
<thead>
<tr>
<th>$g$</th>
<th>$\eta_{0,T_{\text{ref}}}^g$ (\mu Pa s)</th>
<th>$\eta_{0,T_{\text{ref}}}^g / \eta_{0,T_{\text{ref}}}^\text{He}$</th>
<th>$10^3 (d\eta / d\rho) / \eta$</th>
<th>$a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>8.8997 ± 0.0030</td>
<td>0.44891 ± 0.00034</td>
<td>19.2 ± 4.7</td>
<td>0.69</td>
</tr>
<tr>
<td>He</td>
<td>19.8253 ± 0.0002</td>
<td>1.00000 ± 0.00001</td>
<td>-1.1 ± 1.3</td>
<td>0.69</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>11.0631 ± 0.0035</td>
<td>0.55803 ± 0.00031</td>
<td>19.2 ± 1.9</td>
<td>0.88</td>
</tr>
<tr>
<td>Ne</td>
<td>31.7088 ± 0.0100</td>
<td>1.59941 ± 0.00031</td>
<td>1.4 ± 0.1</td>
<td>0.68</td>
</tr>
<tr>
<td>N$_2$</td>
<td>17.7494 ± 0.0048</td>
<td>0.89529 ± 0.00027</td>
<td>6.3 ± 0.6</td>
<td>0.77</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>9.2305 ± 0.0030</td>
<td>0.46559 ± 0.00033</td>
<td>8.2 ± 2.0</td>
<td>0.94</td>
</tr>
<tr>
<td>Ar</td>
<td>22.5666 ± 0.0060</td>
<td>1.13827 ± 0.00027</td>
<td>4.9 ± 0.5</td>
<td>0.85</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>8.1399 ± 0.0028</td>
<td>0.41058 ± 0.00035</td>
<td>-4.9 ± 2.0</td>
<td>0.99</td>
</tr>
<tr>
<td>Kr</td>
<td>25.3062 ± 0.0080</td>
<td>1.27646 ± 0.00032</td>
<td>3.6 ± 0.5</td>
<td>0.92</td>
</tr>
<tr>
<td>Xe</td>
<td>23.0183 ± 0.0072</td>
<td>1.16106 ± 0.00031</td>
<td>2.7 ± 0.2</td>
<td>0.98</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>15.2234 ± 0.0054</td>
<td>0.76788 ± 0.00036</td>
<td>0.6 ± 0.6</td>
<td>0.89</td>
</tr>
</tbody>
</table>

2. Single-capillary viscometers

The molar flow rate $\dot{n}$ of a gas through a capillary with internal radius $r$ and length $L$ depends on temperature $T$ and the pressures just upstream ($p_1$) and downstream ($p_2$) of the capillary as follows [13]:

$$\dot{n} = \frac{\pi r^4 (p_1^2 - p_2^2)}{16LRT\eta_{0,T}^g} C^g \left( T, p_1, p_2 \right)$$

(2)

In Eq. (2), $R$ is the universal gas constant, and $\eta_{0,T}^g$ is the viscosity determined for gaseous substance $g$ at $T$ in the limit of zero pressure. The first factor in Eq. (2) comes from combining ideal-gas compressibility with the Hagen-Poiseuille equation for incompressible flow through a capillary [14], and it estimates the flow rate to within a few percent for a gas near ambient temperature and pressure. The second factor,
contains five terms $c_i^g$ that are usually small corrections to the flow of an ideal gas through a straight capillary. They account for: (1) the density virial coefficients and the viscosity virial coefficient, (2) slip at the capillary wall, (3) the increase in the kinetic energy of the gas as it enters the capillary, (4) gas expansion along the length of the capillary, and (5) the radial temperature distribution within the gas resulting from gas expansion and viscous dissipation. The function $f_{\text{cent}}$ accounts for the centrifugal effect that occurs when the capillary is coiled. It depends on the geometric ratio $r/R_{\text{coil}}$, where $R_{\text{coil}}$ is the radius of curvature of the capillary coil, and the Dean number $De = (r/R_{\text{coil}})^{1/2} Re$, where $Re \equiv 2M\bar{n}/(\pi r\bar{\eta})$ is the Reynolds number; $M$ is the molar mass, and $\bar{\eta}$ is the viscosity at the average pressure defined by Eq. (7) of [13]. Further details about each of the correction terms are given in [13].

The most accurate gas viscosity ratios have been measured near room temperature; here we pay special attention to viscosity ratios at 25 °C of dilute gases relative to that of helium, which we denote as $\eta_{0,T,\text{ref}}^g/\eta_{0,T,\text{ref}}^{\text{He}}$. In general, determining $\eta_{0,T}^g/\eta_{0,T}^{\text{He}}$ with a single-capillary viscometer requires measurements, for both gases, of the molar flow rate $\dot{n}$, the upstream and downstream pressures, and the temperature $T$ of the capillary. One then applies Eq. (2) twice, once for the test gas and once for helium, and forms the ratio of these two equations:

$$\frac{\eta_{0,T}^g}{\eta_{0,T}^{\text{He}}} = \frac{\left(p_1^2 - p_2^2\right)_g}{\left(p_1^2 - p_2^2\right)_{\text{He}}} \frac{\left(1 + \sum_{i=1}^{5} c_i^g\right)}{\left(1 + \sum_{i=1}^{5} c_i^{\text{He}}\right)} \frac{f_{\text{cent}}(De_g, r/R_{\text{coil}}) \dot{n}_g}{f_{\text{cent}}(De_{\text{He}}, r/R_{\text{coil}}) \dot{n}_{\text{He}}}$$  (4)

Equation (4) is accurate when the capillary’s geometry is consistent with the assumptions used to develop the hydrodynamic model. Three of the corrections in Eq.
are proportional to \( r/L \), so the radius-to-length ratio must be small. If the capillary is straight, small deviations of the capillary bore from circularity and uniformity are acceptable because the effective radius \( r \) is determined by fitting to the helium measurement. If a long capillary is wound into a coil, the coil’s radius \( R_{\text{coil}} \) must be sufficiently uniform and well known to accurately calculate the correction function \( f_{\text{cent}} \). The correction increases as \( \varepsilon (De)^4 \), where \( \varepsilon \equiv 1 - y/x \) is a measure of the flatness of the capillary, and \( x \) and \( y \) are the bore’s (unknown) semi-radii. [1,13,15].

Equation (3) includes a correction for slip flow that is proportional to the ratio of the mean free path to the capillary’s radius: \( \lambda/r \), where \( \lambda \) is the mean free path. The calculated correction assumes \( \lambda/r < 1 \). Helium requires special attention because, for a given temperature and pressure, its mean free path is the largest of any gas. More importantly, the momentum accommodation coefficient for helium on smooth quartz glass deviates from unity and was observed to drift from year to year in the same capillary [13].

Another effect sensitive to \( \lambda/r \) is the thermomolecular pressure gradient [16] that can occur when there is a large difference between the temperatures of the capillary and the pressure sensors. Not accounting for this effect will cause errors in \( p_1 \) and \( p_2 \) at sufficiently low pressures.

Determining \( \frac{\eta_{0,\text{ref}}}{\eta_{0,\text{ref}}} \) with a single-capillary viscometer requires a flow meter with a nonlinearity and irreproducibility that are smaller than the desired uncertainty of the viscosity ratio. The flow meter’s absolute uncertainty is less important because
an incorrect calibration factor will cancel out of the factor $\dot{n}_{\text{He}} / \dot{n}_g$ in Eq. (4) and affect only the corrections that are proportional to $Re$ and $De$.

3. Two-capillary viscometers

A two-capillary viscometer, comprising two capillaries in series, can be used to measure the temperature dependence of viscosity ratios with small uncertainty and without the need for a flow meter. May et al. [1,2] developed and used such a viscometer to measure the viscosities of hydrogen, methane, argon, and xenon in the temperature range from 200 K to 400 K. They analysed their measurements with the relation,

$$\eta_{0,T}^g = \eta_{0,T,\text{ref}}^\text{He} \left( \frac{\eta_{0,T}^\text{He}}{\eta_{0,T,\text{ref}}^\text{He}} \right)_{\text{ab initio}} \left( \frac{\eta_{0,T,\text{ref}}^g}{\eta_{0,T,\text{ref}}^\text{He}} \right) R_{T,\text{ref}}^{\text{He}}. \quad (5)$$

Equation (5) has four factors: (i) a reference value $\eta_{0,T,\text{ref}}^\text{He}$ for the viscosity of helium at zero density and 298.15 K, calculated $ab$ initio from quantum mechanics and statistical mechanics [12], (ii) the temperature-dependent ratio $\left( \frac{\eta_{0,T}^\text{He}}{\eta_{0,T,\text{ref}}^\text{He}} \right)_{\text{ab initio}}$, also calculated $ab$ initio [12], (iii) a reference value for the viscosity ratio $\eta_{0,T,\text{ref}}^g / \eta_{0,T,\text{ref}}^\text{He}$ measured at 298.15 K [11], and (iv) a measurement of the temperature-dependent ratio of viscosity ratios,

$$R_{T,\text{ref}}^{\text{He}} = \left( \frac{\eta_{0,T}^g}{\eta_{0,T}^\text{He}} \right) / \left( \frac{\eta_{0,T,\text{ref}}^g}{\eta_{0,T,\text{ref}}^\text{He}} \right). \quad (6)$$

May et al. used a single-capillary viscometer to measure $\eta_{0,T,\text{ref}}^g / \eta_{0,T,\text{ref}}^\text{He}$ and a two-capillary viscometer to measure $R_{T,\text{ref}}^{\text{He}}$ [1,2]. Such an approach is effective because the uncertainties of the theoretical quantities $\eta_{0,T,\text{ref}}^\text{He}$ and $\left( \frac{\eta_{0,T}^\text{He}}{\eta_{0,T,\text{ref}}^\text{He}} \right)_{\text{ab initio}}$ are less
than 0.01 % [12] and because the uncertainties of the measured values of the ratios 
\[ \eta_{0,\text{ref}}^{g}/\eta_{0,\text{ref}}^{\text{He}} \] and \[ R_{T,\text{ref}}^{g,\text{He}} \] are nearly equal to their precisions.

The reference ratio \[ \eta_{0,\text{ref}}^{g}/\eta_{0,\text{ref}}^{\text{He}} \] was measured by a single-capillary viscometer using the techniques and analysis described in [1,2,13], while \[ R_{T,\text{ref}}^{g,\text{He}} \] was measured over the temperature range of interest by the two-capillary viscometer shown in Figure 1. With the upstream capillary’s temperature controlled at the reference temperature of 298.15 K, and the downstream capillary’s temperature controlled at the measurement temperature \( T \), helium and the test gas were flowed alternately through the two-capillary viscometer while the pressures were measured at the ends of both capillaries. Importantly, no flow rate measurements were required to determine \( R_{T,\text{ref}}^{g,\text{He}} \).
Figure 1. Schematic diagram of the two-capillary viscometer used by May et al [1,2]. The impedances $Z_{up}$ and $Z_{down}$ were coiled nickel capillaries with a length of 7 m and an inside diameter of 0.8 mm. The variable impedances $Z_1$ and $Z_3$ were piezoelectric gas leak valves, and $Z_2$ was either a leak valve or a mass flow controller. (Reprinted from [2] with permission of Springer.)

Figure 1 indicates five flow impedances: the upstream and downstream capillaries, denoted respectively as $Z_{up,ref}$ and $Z_{down,T}$, each of which is connected to an upstream and downstream pressure gauge, and the variable impedances denoted as $Z_1$, $Z_2$, and $Z_3$. During a measurement $p_1$ and $p_2$ were maintained at constant, predetermined values by controlling $Z_1$ and $Z_2$. This established a stable but unknown gas flow rate $\dot{n}$ that was identical through both capillaries. If both $\dot{n}$ and $Z_{down,T}$ were known, Eq. (2) could be used to determine the viscosity at the temperature $T$ from accurate measurements of $p_3$ and $p_4$. However, $\dot{n}$ and $Z_{down,T}$ were unknown; therefore, Eq. (2) was applied separately to the upstream and downstream capillaries to eliminate $\dot{n}$ and obtain an expression for the viscosity ratio $\eta_{0,T}^g/\eta_{0,ref}^g$ in terms of $p_1$, $p_2$, $p_3$ and $p_4$. 

water bath at 298.15 K
upstream capillary coil $Z_{up,298}$
ethanol or oil bath at $T$
downstream capillary coil $Z_{down,T}$
He or test gas
bypass
isolation
vacuum pump
Combining that expression for the test gas with a similar expression for the helium measurements yields the working equation:

\[ R_{g, He}^{g, He} = \frac{\left( p_3^2 - p_4^2 \right)_{g}^{g} \left( p_1^2 - p_2^2 \right)_{g}^{g} C_s^g (T, p_3, p_4) C_s^{He} (T, p_1, p_2)}{\left( p_1^2 - p_2^2 \right)_{g}^{g} \left( p_3^2 - p_4^2 \right)_{g}^{g} C_s^g (T, p_1, p_2) C_s^{He} (T, p_3, p_4)} \]  

Equation (7) does not contain the impedance ratio \( Z_{up, Tref}/Z_{down, Tref} \), which depends on temperature through the thermal expansion of the downstream capillary. Instead, Eq. (7) contains the viscosity ratio \( \eta_{He}/\eta_{He, Tref} \), which is known from \( ab\ initio \) calculations. The dimensions of the capillaries appear only in the correction terms of Eq. (3); therefore, approximate values of the dimensions are sufficient for Eq. (7).

May et al. used two coils of electroformed nickel tubing, each with a nominal internal diameter of 0.762 mm, a length of about 7.45 m, in a helical coil with a 0.1 m radius of curvature and a length of 0.04 m [1,2].

Stability and accurate measurements of temperature and pressure are central to the determinations of \( \eta_{He, Tref}/\eta_{He, Tref} \) and \( R_{g, He}^{g, He} \). The nickel capillaries used by May et al. were immersed in stirred liquid baths that controlled their temperatures with an uncertainty of 0.01 K. The flow rates and the viscometer’s design ensured that the temperature of the flowing gas reached the bath’s temperatures before the gas entered each capillary. The pressure transducers had full scales of 300 kPa or 150 kPa, an uncertainty of 0.008 % of full scale (±24 Pa or ±12 Pa), and a resolution of 0.16 Pa.

The experimental quantities of primary importance are the difference pressures across the capillaries, \( \Delta p_{12} \equiv p_1 - p_2 \) and \( \Delta p_{34} \equiv p_3 - p_4 \). Several refinements were used to measure \( \Delta p_{12} \) and \( \Delta p_{34} \) with relative uncertainties of order \( 10^{-4} \). The two pairs of transducers ( which measured \( p_1, p_2, p_3, \) and \( p_4 \)) and the two bypass valves were housed in a temperature controlled enclosure. Before and after every measurement,
the bypass valves were opened to measure the zero-offsets of \( \Delta p_{12} \) and \( \Delta p_{34} \) near the average operating pressures. The measured zero-offsets were used to tare subsequent readings of \( \Delta p_{12} \) and \( \Delta p_{34} \) made while the bypass valves were closed. The pressures \( p_1, p_2 \) and \( p_4 \) were controlled at their set points using the variable impedances \( Z_1, Z_2 \) and \( Z_3 \) and digital proportional-integral algorithms. The pressure set-points were chosen so that for both gases the flow rates and average pressures within the two capillaries were similar. The upstream capillary’s upstream pressure \( p_1 \) was usually fixed near 125 kPa, and its downstream pressure \( p_2 \) was set to four values (between about 100 kPa and 120 kPa) to produce four flow rates ranging from about 4 \( \mu \text{mol}\cdot\text{s}^{-1} \) to 80 \( \mu \text{mol}\cdot\text{s}^{-1} \). The downstream capillary’s downstream pressure \( p_4 \) was then controlled sequentially at six set points between 13 kPa and 75 kPa for each of the four flow rates. This array of 24 measurements per gas per temperature was used to estimate the dependence of the measured values of \( R_{T,\text{ref}}^{g,\text{He}} \) [Eq. (7)] on the Dean number and the small pressure-dependence of the viscosity, as described below.

Automation of the entire apparatus and experimental method, including taring of the pressure transducers was essential because the measurements of \( R_{T,\text{ref}}^{g,\text{He}} \) at each temperature required a time of several hours while the apparatus stepped through two identical sets of \( \{p_2, p_4\} \) conditions, one for helium and one for the test gas. These refinements to the apparatus and experimental method enabled the pressure differences \( \Delta p_{12} \) and \( \Delta p_{34} \) to be controlled and measured to within 0.01 %, with the dominant uncertainty due to the instability (\( \approx 2 \) Pa) in the uncontrolled pressure \( p_3 \).

In many cases the correction factor \( C^x(T, p_1, p_2) \) can be determined with sufficient accuracy that Eq. (7) can be used directly to calculate \( R_{T,\text{ref}}^{g,\text{He}} \). Such cases require that
(a) the Dean number and, hence, the centrifugal flow correction be sufficiently small, and (b) that the following parameters required to evaluate the $c_i^g$ terms for the gas are sufficiently well known: the molar mass $M$, the zero-density viscosity $\eta_0^g$, the density virial coefficients $B$ and $C$, the thermal conductivity, the temperature derivative of the zero-density viscosity $d\eta_0^g/dT$, and the viscosity virial coefficient $B_\eta \equiv \lim_{\rho \to 0} (\partial \eta / \partial \rho)_T$. Of these, it is $B_\eta$ that is least well known, but under certain circumstances the equivalent quantity $b_i^g \equiv \lim_{\rho \to 0} (\partial \eta / \partial \rho)_T / \eta = B_\eta (\partial \rho / \partial p)_T / \eta$ can be measured with a modest uncertainty by the two-capillary viscometer itself.

To determine whether the correction terms in $C^g(T,p_1,p_2)$ are sufficiently accurate, it is useful to calculate the quantity

$$\Xi^g(T) \equiv \frac{\Delta p_{34} \bar{p}_{34}}{\Delta p_{12} \bar{p}_{12}} \frac{C^g(T,p_3,p_4)}{C^g(T_{ref},p_1,p_2)}$$

and test its dependencies on the mean pressure in the downstream capillary, $\bar{p}_{34} \equiv (p_3 + p_4)/2$ and on the Dean number of the flow through the downstream capillary. An incorrect value of $B_\eta$ will cause $\Xi^g$ to vary with $\bar{p}_{34}$. May et al [2] adjusted $B_\eta$ to minimize such variation, and thereby obtained a more accurate value of $B_\eta$.

For gases that have accurately-known density and viscosity virial coefficients, the pressure-dependence of $\Xi^g$ can be taken into account when calculating the correction terms $c_i^g$. However, accounting for the dependence of $\Xi^g$ on the Dean number is more complicated. The correction for centrifugal flow in the hydrodynamic model
extends to $De > 16$ only if the capillary bore is sufficiently circular and uniform. Capillaries that are robust enough to operate over a wide range of temperatures are unlikely to satisfy this criterion, and the lowest order correction to the centrifugal function $f_{\text{cent}}$ in Eq. (2) for a capillary with a slightly elliptical bore is proportional to $(De)^4$ [1,13,15]. Under these circumstances, the value of $R^{4\text{He}}_{T,\text{ref}}$ should not be estimated directly from Eq. (7) but rather from

$$R^{4\text{He}}_{T,\text{ref}} = \lim_{De \to 0} \Xi^{4}(T) / \lim_{De \to 0} \Xi^{\text{He}}(T)$$

(9)

References