CHAPTER 1

Acoustic Techniques for Measuring Transport Properties of Gases

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1.1 Introduction: Acoustic Measurements of Gas Properties

The acoustic resonance frequencies *f* and the resonance half-widths *g* of a gas-filled cavity are functions of the cavity's size and shape, the speed of sound in the gas c, and the thermophysical properties of the gas. In a first approximation, the resonance frequencies *f* depend on the speed of sound; in contrast, the resonance half-widths g are sums of terms that account for energy dissipated by the gas's thermal conductivity λ , shear viscosity η , bulk (or second) viscosity ζ^{\dagger} , and the term g_{mech} , where g_{mech} accounts for energy losses from mechanical effects such as friction in joints, transducer losses, and acoustic radiation outside the cavity. Cavity resonators used for measuring the speed of sound are designed to have narrow resonance peaks so that the resonance frequencies can be determined precisely and so that the frequencies are comparatively insensitive to the transport properties λ , η , and ζ . In contrast, cavity resonators used to measure these transport properties are designed so that the energy dissipated by λ , η , and ζ is much larger than g_{mech}. Consequently, resonators that are optimized to measure transport properties have broad resonance peaks. With reasonable precautions,

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[†]The IUPAC *Green Book* recommends the symbol κ for bulk viscosity, however, for the sake of consistency with previous publications concerning the topic of this chapter ζ will be used herein after.

the measurements of the resonance frequencies and half-widths have very low uncertainties; the uncertainty of acoustic determinations of transport properties is dominated by imperfect modeling/understanding of cavity resonators and g_{mech} .

The sections that follow describe the design and performance of three acoustic resonators that we developed for measurements in gases: one resonator was optimized for measurements of shear viscosity, one was optimized for bulk viscosity measurements. The three resonators are small so that they require only small gas samples whose temperature and pressure are easily controlled over wide ranges, and they are rugged with no moving parts. Using the first resonator, we accurately measured the shear viscosity of hazardous gases at temperatures between 200 K and 400 K and pressures up to 3.4 MPa. With the third resonator, we accurately measured the critical-fluctuation-driven bulk viscosity of xenon on the critical isochore at reduced temperatures 100 times closer to the critical point (290 K and 5.8 MPa) and at frequencies 3000 times lower than ever before.

Of the three transport properties, the shear viscosity is easiest to measure at low densities. Accurate acoustic measurements of the thermal conductivity are more difficult because the dissipation from thermal conduction is usually smaller than that from viscosity by a factor on the order of $(\gamma - 1)$, and $(\gamma - 1) \ll 1$ for polyatomic molecules of interest. (Here $\gamma \equiv C_p/C_V$ is the heat-capacity ratio.) (In Section 1.3, we discuss an exception to this generalization. In a spherical cavity, the acoustic velocity of the radially-symmetric modes is perpendicular to the cavity's walls; therefore these modes are not damped by the shear viscosity.) In low-density gases,¹ the bulk viscosity $\zeta \propto \rho^2$, which vanishes as $\rho \rightarrow 0$; therefore, it is too small to measure. Near the critical point, ζ diverges more strongly than the other transport coefficients; therefore, it dominates acoustic losses and is easy to measure accurately.

1.2 Shear Viscosity Measurements: The Greenspan Viscometer

1.2.1 Description

In 1953, Greenspan and Wimenitz² attempted to determine the viscosity of air from measurements of *f* and *g* in a two-chambered Helmholtz resonator somewhat like the resonator shown in Figure 1.1. Their results deviated relatively from literature data by as much as 38 %. In 1996, we began a program to develop an accurate viscometer based on Greenspan's concept, which we call the Greenspan acoustic viscometer. Since then, we have improved the theory³ and the resonator design^{4–7} to achieve significantly better results; our measurements with the Greenspan viscometer deviate relatively from reference data by less than ± 0.5 %.

The Greenspan acoustic viscometer is a double Helmholtz resonator composed of two gas-filled chambers connected by a tube (or duct)



Figure 1.1 Cross section of a Greenspan viscometer.³ The dotted line AA' indicates the axis of circular symmetry for all parts except the fill capillary. Two cylindrical chambers fitted with source (S) and detector (D) transducers are coupled by a concentric cylindrical duct. The dimensions in millimetres for the viscometer are: $L_d = 31.17$, $r_d = 2.316$, $r_d' = 3.21$, $r_c = 21.02$, $L_c = 21.04$, and $L_i = 10.5$. The fill capillary has an inner radius $r_f = 0.1$ mm (not to scale) and a length $L_f = 80$ mm.

(see Figure 1.1). The fundamental acoustic mode is a low-frequency, low-O mode in which the gas oscillates between the two chambers through the duct. As a characteristic of a Helmholtz acoustic mode, the wavelength of the mode is much longer than the internal dimensions of the resonator. The frequency response of the Helmholtz mode is easy to measure because the mode is non-degenerate and isolated; its frequency is far below the other acoustic modes of the enclosed gas and below the elastic modes of the resonator body. The low frequency leads to a thick boundary layer that reduces the requirement for a fine surface finish compared to the moderatefrequency resonators used for sound speed measurements. The low Q reduces the relative importance of the difficult-to-estimate contributions to the measured half-width g_{meas} and also reduces the need to maintain very high temperature stability. The only requirement is that the transducers have a smooth, well-behaved response (no peaks) in the range $f_{\text{meas}} \pm 4g_{\text{meas}}$ that can be described by a low-order polynomial. The Greenspan viscometer is rugged; it has no moving parts (aside from the minute motion of the transducers) and can be made from corrosion-resistant alloys. In our work, the acoustic transducers, and the "dirty" materials of which they are made, are separated from the test gas by thin metal diaphragms that are machined into the chamber's walls.

In the lowest-order approximation, neglecting dissipation, the gas in the duct and just outside the duct ends moves like a rigid plug with mass $\rho A_d (L_d + 2\delta_i)$ that oscillates back and forth between two identical springs. Here, ρ is the gas density, $A_d = \pi r_d^2$ is the cross-sectional area of the duct, r_d and L_d are the duct radius and length, and the length $\delta_i \approx 0.655 r_d$ is an

inertial end correction that accounts for diverging flow at the end of the duct. As gas flows into a chamber, the pressure in that chamber increases and provides a restoring force, like a spring. The combined stiffness $2\rho c^2 A_d^2/V_c$ of the two springs is a result of the compression and rarefaction of the gas in the chambers. In this level of approximation, the resonance frequency is

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{\text{stiffness}}{\text{mass}}} = c \sqrt{\frac{r_d^2}{2\pi V_c (L_d + 2\delta_i)}},$$
(1.1)

where *c* is the speed of sound in the gas, and V_c is the volume of each chamber. The wavelength of sound (c/f_0) is determined by geometric factors and is independent of the properties of the gas. For the resonator described in ref. 3, eqn (1.1) predicts $f_0 = (0.9299 \text{ m}^{-1}) \times c$, which is a few hundred hertz for most gases near ambient temperature. However, the corresponding wavelength (approximately 1.075 m) is the same for all gases. Heat and momentum diffusion near the cavity walls decrease the measured resonance frequency f_{meas} from the estimate in eqn (1.1) by a few percent, but eqn (1.1) is sufficient as a design aid.

For the Helmholtz mode, the acoustic velocity is greatest in the duct; therefore, shear in the gas flow near the duct's wall dissipates most of the acoustic energy. If this were the only dissipation mechanism, the gas's shear viscosity η could be determined from a measurement of the resonance frequency f_{meas} and the quality factor Q_{meas} using the expression

$$\eta \approx \frac{\rho \pi r_{\rm d}^2 f_{\rm meas}}{Q_{\rm meas}^2} \left(\frac{1 + 2\delta_{\rm i}/L_{\rm d}}{1 + 2\varepsilon_{\rm r0} r_{\rm d}/L_{\rm d}} \right)^2.$$
(1.2)

The numerically-calculated parameters δ_i and ε_{r0} describe, respectively, the inertial and dissipative effects of the duct ends. However, heat transport between the oscillating gas and the metal wall of the resonator causes significant acoustic energy dissipation; therefore eqn (1.2) overestimates η . The fractional overestimate is 0.44 $(\gamma - 1) Pr^{-1/2}$ for the viscometer described in ref. 3, where $Pr = \eta C_p / \lambda$ is the Prandtl number, and λ is the thermal conductivity of the gas. This overestimate ranges from 36%, for monatomic gases such as argon and helium, to as little as 5 % for typical polyatomic gases. Fortunately, the design of the Greenspan viscometer is such that, in most cases, the uncertainty in the thermal conductivity of the gas is a small contribution to the uncertainty of the deduced viscosity. For example, the thermal conductivities of helium and argon have such low relative uncertainties, \pm 0.002 % and \pm 0.02 % respectively, that their contribution to the uncertainty of the viscosity measurement is negligible, despite the rather large effect of heat conduction. For a typical polyatomic molecule with $\gamma \approx 1.1$ and $Pr \approx 0.7$, a relative uncertainty in the thermal conductivity of ± 10 % contributes only about ± 0.2 % to the relative uncertainty of the deduced viscosity.

The next level of approximation includes the most important dissipation mechanisms that contribute to the half-width g_{meas} and the resonance

line shape. In this approximation, the inverse of the resonance quality factor $Q^{-1} \equiv 2g_{\text{meas}}/f_{\text{meas}}$ is the sum of three terms:

$$\frac{1}{Q} = \frac{\delta_{\rm v}}{r_{\rm d}} \cdot \frac{L_{\rm d} + 2\varepsilon_{\rm r}r_{\rm d}}{L_{\rm d} + 2\delta_{\rm i}} + (\gamma - 1)\frac{\delta_{\rm t}S_{\rm c}}{2V_{\rm c}} + (\gamma - 1)\frac{C_{\rm relax}}{C_p}\frac{2\pi f_{\rm meas}\tau_{\rm relax}}{1 + (2\pi f_{\rm meas}\tau_{\rm relax})^2}.$$
 (1.3)

The first term in eqn (1.3) is the damping that occurs in the viscous boundary layer at the wall and near the ends of the main duct. Here, $\delta_{\rm v} =$ $\left[D_{\rm v}/(\pi f_{\rm meas})\right]^{1/2}$ is the thickness of the viscous boundary layer in oscillating flow at frequency f_{meas} , where $D_{\rm v} = \eta/\rho$ is the viscous diffusivity (also called the kinematic viscosity). The second term is the damping from heat conduction that occurs near the wall of the chambers, which have surface area S_c. The length $\delta_t = \left[D_t / (\pi f_{\text{meas}}) \right]^{1/2}$ is the thickness of the thermal boundary layer, where $D_t = \lambda / (\rho C_p)^{\dagger}$ is the thermal diffusivity. Although δ_v and δ_t differ only by the factor $Pr^{-1/2}$, the second term is significantly reduced by the smaller surface area-to-volume ratio S_c/V_c in the chamber and the factor $(\gamma - 1)$, which is small for polyatomic molecules. The third term in eqn (1.3) is important for certain gases (e.g. CH_4 , CO_2) that have symmetries such that many intermolecular collisions are required for their internal degrees of freedom to adjust to the temperature change associated with the acoustic oscillation. In such gases, the acoustic dissipation is characterized by the product $C_{relax}\tau_{relax}$, where C_{relax} is the heat capacity associated with the slowly relaxing degrees of freedom and τ_{relax} is the relaxation time, which is proportional to ρ^{-1} .

The next section describes the model for acoustic response of the Greenspan viscometer and how its measurement is used to determine the gas viscosity. Ref. 3 contains more details and a derivation of the model.

1.2.2 Basic Theory

In a Greenspan viscometer, a continuous sound source located in one chamber generates an acoustic wave at frequency *f* that is reflected back and forth between the chambers through the duct. We assume the time dependence is $e^{i\omega t}$ with $\omega = 2\pi f$. When the frequency is such that a reflected wave arrives back at the source in phase with the wave being generated there, resonance occurs. Acoustic waves in long gas-filled ducts are governed by the equations first proposed by Kirchhoff,⁸ whose classic paper includes a description of the effects of the coupled acoustic, thermal, and vorticity waves in ducts of circular cross section. The low-frequency (long-wavelength) limit of Kirchhoff's solutions is generally attributed to Crandall.⁹ Below the cutoff frequency for transverse modes in a duct, only plane waves can propagate. In a duct with a circular cross section, this limit corresponds to wavelengths greater than about 1.7 times the duct diameter, *i.e.* about 8 mm for the duct

[‡]The IUPAC *Green Book* recommends the symbol *a* for thermal diffusivity, however, for the sake of consistency with previous publications concerning the topic of this chapter D_t will be used herein after.

in Figure 1.1, which is much shorter than the wavelength of the natural mode of the Greenspan viscometer.

Low-frequency sound wave propagation in a duct is described accurately by a set of differential equations for lossy transmission lines that relate the acoustic pressure p and volume velocity U. When there is an acoustic source with frequency f and volume velocity U_0 in one chamber (chamber 1), a steady-state acoustic pressure p_2 develops in the other chamber (chamber 2). Finite-length transmission lines are conveniently described by an equivalent circuit containing lumped acoustic impedances in a T-network. The complete equivalent circuit we use to model the Greenspan viscometer, shown in Figure 1.2, contains a T-network for each half of the central duct (split by the symmetrically-located fill capillary) with additional impedances that model the effects of the duct ends (Z_{end}), the chambers (Z_v), and the fill capillary (Z_c). The acoustic response of the Greenspan viscometer p_2/U_0 is a complex-valued function of frequency that contains the line shape of the Helmholtz resonance.

The acoustic response based on the equivalent circuit is

$$\frac{p_2}{U_0} = \frac{Z_b^2 Z_c Z_V^2}{D_1 D_2},\tag{1.4a}$$

where the factors in the denominator are

$$D_1 = (Z_b + Z_a)(Z_V + Z'_a) + Z_b Z_a$$
(1.4b)

$$D_2 = Z_b Z_V + 2Z_c (Z_b + Z_V) + Z'_a (Z_b + 2Z_c) + Z_a (Z_b + Z_V + Z'_a).$$
(1.4c)

Eqn (1.4a) is the basis of the complex resonance function used in the data analysis. The Helmholtz resonance condition is defined as the complex frequency $F_{\rm H} = f_{\rm H} + ig$ for which $D_1 = 0$, where $f_{\rm H}$ is the measured resonance frequency and g is the resonance half width. [2g is defined as the fullwidth at half-maximum of the energy response function. The quality factor Qis defined as $Q = f_{\rm H}/(2g)$.] The acoustic pressure for the Helmholtz mode is an odd function of distance from the resonator's mid-plane, so there is a pressure node at the entrance to the capillary; therefore the resonance frequency and the line shape for the Helmholtz mode are independent of $Z_{\rm c}$. The effect that $Z_{\rm c}$ has on the total acoustic response in eqn (1.4) in the



Figure 1.2 Equivalent circuit for the Greenspan viscometer shown in Figure 1.1 and described by eqn (1.4). The centrally-located fill capillary has acoustic impedance Z_c .

vicinity of the Helmholtz mode is to change the "background" due to the tails of other modes, which is weakly dependent on frequency.

Within the chambers, the gas compressibility in the long wavelength limit considered here is isothermal near the walls and adiabatic far from the walls. The acoustic impedance of each chamber calculated from the average compressibility within the chamber is given by the expression¹⁰

$$Z_{V} = \frac{\rho c^{2}}{i\omega V_{c}} \frac{1}{\sqrt{1 + \frac{1}{2}(1 - i)(\gamma - 1)S_{c}\delta_{t}/V_{c}}},$$
(1.5)

which includes the effect of heat conduction over the chamber's surface area S_{c} .

The T-network impedances shown in Figure 1.2 are given by the expressions

$$Z_{a} = Z_{0} \tanh(\Gamma L_{d}/4), Z_{b} = Z_{0}/\sinh(\Gamma L_{d}/2), \qquad (1.6a)$$

$$Z'_{\rm a} = Z_{\rm a} + Z_{\rm end}$$
, and $Z_{\rm end} = \frac{\rho\omega}{A_{\rm d}} (i\delta_{\rm I} + \delta_{\rm R}).$ (1.6b)

In eqn (1.6), the characteristic impedance Z_0 and the propagation parameter Γ for waves in the duct are given by the expressions

$$Z_0 = \frac{\rho c}{A_{\rm d}} \frac{1}{\sqrt{[1 + (\gamma - 1)F_{\rm t}](1 - F_{\rm v})}}$$
(1.7a)

and

$$\Gamma = \frac{\mathrm{i}\omega}{c} \sqrt{\frac{1 + (\gamma - 1)F_{\mathrm{t}}}{1 - F_{\mathrm{v}}}}.$$
(1.7b)

The complex-valued quantity F_x is the loss function,

$$F_{\rm x}(\kappa_{\rm x}) = \frac{2J_1(\kappa_{\rm x})}{\kappa_{\rm x}J_0(\kappa_{\rm x})},\tag{1.8}$$

which accounts for viscous dissipation (x = v) or thermal dissipation (x = t) near the wall of a circular duct. Here, J_0 and J_1 are Bessel functions of order 0 and 1, respectively, and $\kappa_x = (1 - i)r_d/\delta_x$ with $\delta_v = (2D_v/\omega)^{1/2}$ and $\delta_t = (2D_t/\omega)^{1/2}$.

The lengths $\delta_{\rm I}$ and $\delta_{\rm R}$ in eqn (1.6b) are the inertial and resistive end corrections, respectively, for the main duct. These lengths have been evaluated numerically.¹¹ To first order in $\delta_{\rm v}$ the resistive length is

$$\delta_{\rm R} = \varepsilon_{\rm r} \delta_{\rm v} \tag{1.9}$$

When the duct ends are square, the coefficient ε_r varies weakly with δ_v/r_d according to

$$\varepsilon_{\rm r} = \varepsilon_{\rm r0} + \varepsilon_{\rm r1/3} (\delta_{\rm v}/r_{\rm d})^{1/3} + \varepsilon_{\rm r1} (\delta_{\rm v}/\nu_{\rm d}). \tag{1.10}$$

For the geometry of the viscometer described in ref. 3, the coefficients were evaluated numerically to be $\varepsilon_{r0} \approx 0.987$, $\varepsilon_{r1/3} \approx -0.348$, and $\varepsilon_{r1} \approx 1.15$. The constant term ε_{r0} is sensitive to the shape of the duct ends. Rounding the sharp edges decreases ε_{r0} and a slight burr can increase it. When the Greenspan viscometer is used for absolute measurements, the sensitivity of ε_{r0} to the geometry of the duct ends contributes to the uncertainty in the measured viscosity. In practice, we can adjust ε_{r0} to improve the agreement of the experimental values of the viscosity of helium with the accurately known theoretical values.¹³ In ref. 3, we increased ε_{r0} by 4% to 1.03. It follows from eqn (1.2) that a relative uncertainty in ε_{r0} of 4% contributes an uncertainty of 1% to the viscosity measurement.

The inertial end correction δ_{I} is, to first order in δ_{v} ,

$$\delta_{\rm I} = \delta_{\rm i} + \varepsilon_{\rm i} \delta_{\rm v}.\tag{1.11}$$

As noted previously, $\delta_i \approx 0.655 r_d$ for the experimental resonator discussed in ref. 3; δ_I differs from this by a viscous boundary layer correction term and hence provides a more accurate representation of the inertial end effects. Note that the numerically-calculated value $\varepsilon_i \approx 0.86$ is somewhat smaller than the calculated value of $\varepsilon_{r0} \approx 0.987$. Improved experimental agreement was obtained with a modest increase to $\varepsilon_i \approx 0.96$.

The fill capillary is a duct that is terminated with impedance Z_t . We model the capillary as an acoustic transmission line with characteristic impedance Z_{0f} and propagation parameter Γ_f given by eqn (1.7) and (1.8) with r_d replaced by r_f . In this model the impedance Z_c for the fill capillary is

$$Z_{\rm c} = Z_{\rm 1f} + Z_{\rm e1f} + \frac{Z_{\rm 2f}(Z_{\rm 1f} + Z_{\rm e2f} + Z_{\rm t})}{Z_{\rm 2f} + Z_{\rm 1f} + Z_{\rm e2f} + Z_{\rm t}},$$
(1.12)

where the T-network elements Z_{1f} and Z_{2f} have the same form as Z_a and Z_b , respectively, in eqn (1.6a) with Z_0 replaced by Z_{0f} , Γ replaced by Γ_f , and $L_d/2$ replaced by L_f . The impedances Z_{e1f} and Z_{e2f} account for the end effects at the junction with the main duct and at the termination, respectively; they have the same form as Z_{end} in eqn (1.6b) with A_d , δ_I , and δ_R replaced by A_f , δ_{If} and δ_{Rf} , respectively. The lengths δ_{If} and δ_{Rf} describe the end corrections for the fill capillary, similar to δ_I and δ_R in eqn (1.9) and (1.11), but with r_d replaced with r_f . These corrections are negligible provided that $r_f/L_f \ll 1$. The capillary end effect impedances are small compared to Z_{1f} by a factor that is proportional to r_f/L_f , which is about 0.001 for the viscometer in Figure 1.1. If the capillary is terminated by a volume, such as a closed valve, the impedance Z_t can be approximated by eqn (1.5) using suitable values for the volume and surface area. However, if the termination volume is large compared to $A_f \times$ wavelength (as is usually the case), then Z_t is small compared to Z_{0f} , and sufficient accuracy is achieved by setting $Z_t = 0$.

1.2.3 Experimental Results

The Helmholtz mode response function and the supporting quantities in eqn (1.4) to (1.12) constitute a physical model of the sound pressure that is

generated by a continuous sound source as a function of frequency in terms of the properties of the gas medium. The source transducer generates a volume displacement in one chamber that is proportional to the applied source voltage V_s , which is the amplified output of a sinusoidal function generator. A microphone in the other chamber outputs a voltage signal V_{mic} that is proportional to the acoustic pressure there. The voltages V_s and V_{mic} are measured with two dual-phase lock-in amplifiers that are referenced to the function generator. We measured the response at 21 uniformly-spaced frequencies spanning the range $\pm 2g$ about the center frequency f_H in steps of increasing and then decreasing frequency. We computed the complex ratio $V_{mic}/V_s = u + i\nu$ at each frequency and fit the data by adjusting the speed of sound *c* and the viscous diffusivity D_v using the function

$$u + \mathrm{i}v = A' \frac{\tilde{Z}_{\mathrm{b}}^2 \tilde{Z}_{\mathrm{c}} \tilde{Z}_V^2}{\tilde{D}_1 \tilde{D}_2} + B' + C' (f - f'') + D' (f - f'')^2, \qquad (1.13)$$

where A', B', C', and D' are adjustable complex-valued parameters, and f'' is approximately the average frequency in the data set. (The parameter f'' is not adjusted; it is included in eqn (1.13) to increase the reliability of the datafitting routine.) The parameter A' is an arbitrary scale factor that depends on the sensitivity of the microphone and the strength of the source. The dimensionless expression multiplying A' is the acoustic response in eqn (1.4) with each of the impedances reduced by Z_0 (indicated by the tilde) to remove the explicit dependence on ρc . The background parameters B', C', and D'account for electrical cross talk between the source and detection circuits and for the frequency response of the transducers. C' and sometimes D' were included in the fit when justified by an F-test. Figure 1.3 compares the measured response function of a Greenspan viscometer filled with argon to a least-squares fit using eqn (1.13) with 8 adjustable parameters. The response function has been normalized by the maximum value. The deviations from the fit are random and have a root-mean-square (RMS) of 0.006%, which shows that eqn (1.13) describes the measured response function extremely well.

Researchers at NIST measured the viscosity of 16 gases, see Table 1.1, using Greenspan viscometers that are similar in size to the design in Figure 1.1.^{4–7,12} In principle, the Greenspan viscometer is an absolute instrument dependent on accurate dimensional measurements and numerically-calculated parameters for the duct end corrections. In practice, the instrument must be calibrated with a reference gas such as helium or argon (due to difficult-to-measure details at the duct's ends, irregularities in the shape of the duct along its length, or crevices at the seals in the chambers).

Figure 1.4 shows the viscosity of argon, helium, xenon, nitrogen, and methane⁴ measured with a Greenspan viscometer before and after calibration compared to reference values. In order to calibrate the particular resonator used in ref. 4, we adjusted the resistive end correction ε_{r0} and the surface area of the chambers to minimize the RMS deviations in Figure 1.4a. The calibration reduced ε_{r0} from the predicted value of 0.972 to 0.939 and increased the chamber surface area by the fractional amount (1.19 μ m/ δ_t),



Figure 1.3 The acoustic response of a Greenspan viscometer filled with argon at 280 K and 1 MPa. The measured ratio $V_{mic}/V_s = w$ was fit using eqn (1.13) with 8 adjustable parameters, where V_{mic} is the vector signal from the microphone and V_s is the vector source excitation voltage. V_{mic} and V_s were measured using two dual-phase lock-in amplifiers with a common reference. The in-phase (—) and quadrature (– –) components of the fit, normalized by the maximum amplitude $|w_{max}|$, are plotted on the left axis as a function of frequency *f*. The normalized deviations from the fit ($w - w_{fit}$)/ $|w_{max}|$ for the in-phase, \bigcirc , and quadrature, \triangle , data are plotted on the right axis with the fit as the baseline. The 84 data points were acquired at 21 equally-spaced frequencies over the range $f_{meas} \pm 2g_{meas}$, where $f_{meas} = 285.89$ Hz and $g_{meas} = 2.91$ Hz. The root-mean-square of the deviations is 6×10^{-5} .

which ranged from 1 % to 5 %. We speculate that the surface area correction was due to the roughness of the chamber surface or a crevice where the chambers and diaphragms were attached. Subsequent viscometers^{5–7} with polished interior surfaces and diaphragms that were machined in place did not require a surface area calibration.

Figures 1.4c and 1.4d compare literature data with measurements of the viscosity and speed of sound made with a Greenspan viscometer⁵ that was calibrated with helium using *ab initio* viscosity values.¹³ The viscosity results are all within ± 0.5 % of the literature values. Most of the speed-of-sound results are within ± 0.03 % of the literature values. However, the results for C₂F₆ and SF₆ have larger deviations from literature values at the higher pressures on the 300 K isotherm where both C₂F₆ and SF₆ approach their critical points. Near critical points, all thermodynamic properties (including the speed of sound) are particularly sensitive to impurities. Therefore, the larger deviations resulted from differences in the concentrations of impurities in our gases and the gases used for the literature studies.

Table 1.1	Summary of gases studied using a Greenspan viscometer. The
	temperature range ΔT , maximum pressure P_{max} , and publication
	reference are listed for each compound. Mixture components are
	specified as mole fraction.

Compound	$\Delta T/\mathrm{K}$	P _{max} /MPa	
Helium	298 to 348	3.2	a,b,c
Argon	225 to 373	3.4	a,b,c
Xenon	298.15	1.1	а
0.47 Helium-0.53 Xenon	250 to 375	1.8	а
Hydrogen	225 to 400	3.3	d
Nitrogen	298.15	3.4	a,b,c
Carbon monoxide	225 to 375	2.5	С
Carbon dioxide	225 to 375	2.5	С
Nitrous oxide	200 to 375	3.4	е
Ammonia	300 to 375	3.4	С
Nitrogen trifluoride	225 to 375	3.4	е
Methane	293.15	3.3	<i>a,b,c</i>
Carbon tetrafluoride	200 to 400	3.4	b
Silicon tetrafluoride	215 to 375	2.5	С
Sulfur hexafluoride	298.15	1.7	<i>b</i> , <i>c</i>
Hexafluoroethane	225 to 375	3.1	b
Propane	293 to 373	3.4	b,c
Octofluorocyclobutane	300 to 375	1.6	С

^aJ. Wilhelm, K.A. Gillis, J. B. Mehl and M. R. Moldover, Int. J. Thermophys., 2000, 21, 983. ^bJ.J. Hurly, K.A. Gillis, J.B. Mehl and M.R. Moldover, *Int. J. Thermophys.*, 2003, 24, 1441.

^cA.F. Estrada-Alexanders and J.J. Hurly, *J. Chem. Thermodynamics*, 2008, **40**, 193.

^dJ.J. Hurly and M. R. Moldover, private communication.

^eJ.J. Hurly, Int. J. Thermophys., 2004, 25, 625.

Figure 1.5 compares literature data^{14,15} for the zero-density limit of viscosity of hydrogen with measurements made with the Greenspan viscometer. The agreement is excellent throughout the temperature range 225 K to 400 K.

Thermal Conductivity 1.3

In principle, the thermal conductivity of dilute gases can be deduced from the widths of the radially-symmetric acoustic modes of a spherical or nearly spherical ("quasi-spherical"), gas-filled cavity of known radius *a*. For such modes, the half-width is a sum of three terms:

$$\frac{g}{f} = \frac{(\gamma - 1)\delta_{\rm t}}{2a} \left[1 - \frac{(2\gamma - 1)\delta_{\rm t}}{a} \right] + \left(\frac{\pi f \delta_{\rm t}}{c}\right)^2 \left[(\gamma - 1) + \frac{4}{3}Pr \right] + \frac{g_{\rm mech}}{f}.$$
 (1.14)

The first term in eqn (1.14), accounts for heat exchange between the wall of the cavity and the gas; the second term accounts for attenuation of sound throughout the volume of the cavity; the third term accounts for mechanical losses, and we have assumed the bulk viscosity $\zeta \equiv 0$. At low densities (below



Figure 1.4 Viscosities η of several gases measured in the Greenspan viscometer compared to reference values as a function of pressure p (a and b) and amount of substance density ρ (c and d). Fractional deviations from reference values as a function of pressure (a) before calibration and (b) after calibration.⁴ \blacktriangle , argon at T=298 K; \bigtriangledown , argon at T=348 K; \triangle , methane at T=298 K; \bigtriangledown , methane at T=298 K; \bigcirc , helium at T=298 K; \diamond , helium at T=348 K; \bigcirc , nitrogen at T=298 K; and \bigcirc , xenon at T=298 K. Fractional deviations of measured (c) viscosities and (d) sound speeds near T=300 K from reference values as a function of density.⁵ +, argon; \bigtriangledown , helium; \triangle , nitrogen; \bigcirc , sulfur hexafluoride; \diamondsuit , methane; \bigcirc , tetrafluoromethane; \blacksquare , hexafluoroethane; and \Box , propane.



Figure 1.5 The viscosity η of hydrogen at zero density plotted as a function of temperature *T*. (a) \bullet , Hurly¹² with a Greenspan viscometer; \triangle , May *et al.*¹⁵; ∇ , Kestin and Yata.¹⁴ (b) Deviations of the measured values from May *et al.*¹⁵

a few hundred 100 kPa at ambient temperature), the first two terms in eqn (1.14) diverge as (δ_t/a) and $(\delta_t/a)^2$, while the third term g_{mech} approaches zero as a linear function of the pressure, albeit with a complicated frequencydependence. Therefore, eqn (1.14) can be used to determine the thermal conductivity of a gas, provided that a crude estimate of the Prandtl number *Pr* is available and provided that γ is known, for example from measurements of the acoustic resonance frequencies of the same gas-filled cavity. Eqn (1.14) is consistent, within 0.002 g/f, with extraordinarily careful measurements of g/f using argon- and helium-filled guasi-spherical cavities that were made to re-determine the Boltzmann constant.¹⁶ Despite this success, spherical cavities and eqn (1.14) cannot be used to easily determine the thermal conductivities of process gases even though such data would be useful to manufacturers and users of thermal mass flow controllers. The difficulty in applying eqn (1.14) to process gases at low densities is that $(\gamma - 1)$ for process gases is only 1/5 to 1/10 of $(\gamma - 1)$ for helium and argon, which is 0.67 at low densities. Therefore, using eqn (1.14) to determine the product $(\gamma - 1) (\delta_t / a)$ for process gases is subject to 5 to 10 times greater uncertainties from g_{mech} and *Pr*. As the density is increased, separating the thermal losses from the mechanical losses becomes increasingly difficult because g_{mech}/f increases as ρc^2 while δ_t / a decreases as $[\lambda / (\rho C_n c)]^{1/2}$. Therefore, using a spherical cavity and eqn (1.14) to measure thermal conductivity is not promising.

In an effort to develop an acoustic method for thermal conductivity measurements,¹⁷ we designed a cylindrical resonator containing a metal honeycomb lattice aligned with cylinder's axis, as shown in Figure 1.6a, that increases the thermal losses for some modes relative to viscous losses and mechanical losses. For even-numbered longitudinal modes, which have a temperature antinode at the honeycomb, the effective area for heat conduction is increased by a factor of $(a/r_{\rm h})(l/\lambda_{\rm a})$ where $r_{\rm h}$ is the hydraulic radius of one honeycomb cell (which must be larger than δ_t and δ_y ; a is the radius of the cylindrical cavity; λ_a is the wavelength of sound; and *l* is the length of the honeycomb (which must be less than $\approx \lambda_a/4$). Figure 1.6b (top) shows the measured half-widths g_{meas} for several modes and gases at constant temperature as a function of δ_t/r_h (for even-numbered modes) or δ_v/r_h (for odd-numbered modes), where r_h is the hydraulic radius of a honeycomb cell. The data span a factor of 50 in $g_{\rm meas}$ and a factor of 10 in $\delta_{\rm t}$ for the three gases shown. The fractional deviations between the measurements and our acoustic model for all three gases are within ± 2.5 % of a single function of δ_t/r_h that underestimates g_{meas} by 10% at high density (small δ_t/r_h) and overestimates g_{meas} by 4 % at low density (large δ_t/r_h). [See Figure 1.6b (bottom).] The results from this cavity at low densities were puzzling because the measured values of the half-widths were smaller than the calculated values. This shows that our model for the cavity containing a honeycomb is not accurate. We believe that the honeycomb concept should be explored further.



Figure 1.6 (a) A sectioned view of a cylindrical resonator containing a honeycomb lattice (the resonator's end plates are not shown). (b) Odd-numbered longitudinal modes have a velocity antinode within the honeycomb; they are more sensitive to η than corresponding modes without the honeycomb, and their half-widths are plotted as a function of δ_v/r_h , where r_h is the hydraulic radius of a honeycomb cell. Even-numbered longitudinal modes have pressure and temperature antinodes within the honeycomb; they are more sensitive to λ than corresponding modes without the honeycomb, and their half-widths are plotted as a function of δ_v/r_h .

1.4 Bulk Viscosity Measurements Near the Liquid–Vapor Critical Point

The bulk viscosity ζ is a transport coefficient that characterizes damping of volume changes of a fluid. The quantity $-\zeta \nabla \cdot \mathbf{u}$, which appears in the relation between the stress tensor and the rate-of-shear tensor, represents a stress, due to internal relaxation processes, that opposes the rate of change of volume. These relaxation processes govern the energy exchange between translational degrees of freedom (the acoustic mode) and other internal modes of the fluid, such as molecular vibrations, metastable intermolecular bound states, or critical fluctuations. An acoustic wave in a relaxing medium loses a fraction $\omega \zeta / (\rho c^2)$ of its energy per cycle due to bulk viscosity.

For a low-density gas of hard spheres, kinetic theory predicts $\zeta \propto \eta \rho^2$, which vanishes as $\rho \rightarrow 0$. For this reason, ζ is often ignored when considering the transport properties of noble gases such as xenon. In the liquid

state near the triple point of xenon, (ζ/η) is about 0.3; however, ζ is difficult to measure because liquids are not very compressible compared with the walls of the cavity.¹⁸ However, ζ can become much larger than η , particularly in polyatomic gases that require many collisions to equilibrate their internal degrees of freedom with their translational degrees of freedom. For such gases, there is a peak in the sound attenuation when $\omega \tau_{\text{relax}} \approx 1$, where τ_{relax} is the relaxation time that characterizes the equilibration between the internal and translational degrees of freedom.

The attenuation α_{λ} of a sound wave propagating in free space over a distance of one wavelength is given by

$$\alpha_{\lambda} = \frac{\pi\omega}{c^2} \left[(\gamma - 1)\frac{\lambda}{\rho C_p} + \frac{4}{3}\frac{\eta}{\rho} + \frac{\zeta}{\rho} + (\gamma - 1)\frac{c^2}{\omega}\frac{C_{\text{relax}}}{C_p}\frac{\omega\tau}{1 + (\omega\tau)^2} \right]$$
(1.15)

where the first two terms constitute the "classical attenuation" due to thermal conduction and viscous losses within the sound wave itself. The third term is the attenuation from bulk viscosity explicitly as a function of ζ , whereas the last term describes the bulk viscosity of a single relaxing mode. The volume processes described in eqn (1.15) also increase the half-widths of resonances in a gas-filled cavity by the amount $g_b = f \alpha_{\lambda}/(2\pi)$.

In a fluid at its critical density ρ_c the characteristic size of equilibrium density fluctuations (the so-called the correlation length) diverges as the critical temperature T_c is approached with the universal power law $\xi \propto$ $(\Delta T^*)^{-0.63}$, where $\Delta T^* \equiv (T - T_c)/T_c$. The dynamic behavior of the fluid's thermophysical properties in the critical region is determined by a characteristic lifetime $\tau \propto (\Delta T^*)^{-1.93}$ for fluctuations of size ξ . The bulk viscosity arises from the dynamic response of critical fluctuations, and at zero frequency it diverges as $\zeta \propto (\Delta T^*)^{-1.93}$ as $\Delta T^* \to 0$, which is a much stronger divergence than the divergence of the thermal conductivity $\left[\lambda \propto (\Delta T^*)^{-0.57}\right]$ or of the shear viscosity $\left[\eta \propto (\Delta T^*)^{-0.069}\right]$. The bulk viscosity is a function of the product $\omega\tau$. At low frequency, such that $\omega\tau \ll 1$ in the critical region, the bulk viscosity exhibits universal power-law behavior. When $\omega \tau \sim 1$, the bulk viscosity deviates from the universal power law, an indication that the fluctuations are not in equilibrium. When $\omega \tau \gg 1$, the bulk viscosity approaches its maximum, non-universal limit. Low-frequency sound waves reach the condition $\omega \tau = 1$ closer to T_c and deeper into the asymptotic critical regime than do high-frequency sound waves.

Acoustic resonators have been rarely used to study liquid-vapor critical phenomena for two reasons: (1) the usual theory of acoustic resonators does not fully account for the critical behavior of the thermophysical properties, and (2) at equilibrium, near-critical fluids stratify in Earth's gravity, so the speed of sound becomes a function of height in the sample. We developed a theory of acoustic resonators that is appropriate for near-critical fluids, and we greatly reduced stratification by stirring the fluid.



Figure 1.7 (a) Horizontal cross-section of a cavity resonator that has well-isolated acoustic modes spanning a wide frequency range. (b) Acoustic resonances when the cavity is filled with xenon near its critical density and critical temperature. In the Helmholtz (H) mode at 120 Hz, the xenon oscillates through the reentrant tube connecting two circular, cylindrical chambers (16 mm diameter, 48 mm long and 23.5 mm diameter, 22 mm long). In the longitudinal modes (L1,...,L5), the xenon oscillates in plane waves along the 48 mm-long cylinder.^{19,20}

We developed an acoustic resonator that was optimized for measurements of bulk viscosity in xenon (BVX) near its critical point.^{19–21} Figure 1.7a shows a horizontal cross section through the resonator. Ref. 19 describes the BVX resonator in more detail. The resonator had two horizontal cylindrical chambers oriented at right angles to each other and connected by a small cvlindrical tube. The asymmetric design yields a spectrum with a lowfrequency Helmholtz mode (H) and five longitudinal modes (L1,...,L5) that span a factor of 27 in frequency (see Figure 1.7b). The lowest frequency we measured, $f_{\rm H} \approx 120$ Hz near $T_{\rm c}$, was 3000 times lower than previous work.^{22,23} The lower frequencies and the reduced density stratification, which we achieved by stirring the xenon, enabled our measurements to probe deeper into the asymptotic critical region than ever before. Figure 1.8a shows an example of our measured dissipation (Q^{-1}) as a function of reduced temperature $(T - T_c)/T_c$ for the lowest frequency (120 Hz) and the highest frequency (3.8 kHz) that we studied. The measured dissipation is a combination of bulk viscosity and dissipation in the thermal boundary layer. The dashed lines show the dissipation due to bulk viscosity predicted by theory. Figure 1.8b shows the bulk viscosity that is consistent with our measurements as a function of reduced temperature. The dashed line is the bulk viscosity at zero frequency, which exhibits the asymptotic power law behavior. At finite frequency, the bulk viscosity deviates from the power law when $\omega \tau \approx 1$, which occurs at successively higher reduced temperatures as the frequency increases.



Figure 1.8 (a) For the resonator in Figure 1.7, Q^{-1} increases as the critical temperature T_c is approached. The dashed curves show the contribution to Q^{-1} from the bulk viscosity ζ at 120 Hz (H mode) and 3.8 kHz (L5 mode). The solid curves and the measurements (\bigcirc , \blacksquare) are the sum of the dashed curves and surface contributions to Q^{-1} . (b) The real part of the bulk viscosity ζ of xenon at three frequencies. At zero frequency, $\zeta \propto [(T - T_c)/T_c]^{-1.93}$; at non-zero frequencies, ζ levels off when $\omega \tau \approx 1$. Near the critical point, $\zeta \gg \lambda/C_p \gg \eta$.¹⁹⁻²¹

References

- 1. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*, 2nd edition, Wiley & Sons, Inc., New York, 1964, 644–645.
- 2. M. Greenspan and F. N. Wimenitz, NBS Report, 1953, 2658.
- 3. K. A. Gillis, J. B. Mehl and M. R. Moldover, *J. Acoust. Soc. Am.*, 2003, 114, 166.
- 4. J. Wilhelm, K. A. Gillis, J. B. Mehl and M. R. Moldover, *Int. J. Thermo-phys.*, 2000, **21**, 983.
- 5. J. J. Hurly, K. A. Gillis, J. B. Mehl and M. R. Moldover, *Int. J. Thermophys.*, 2003, **24**, 1441.
- 6. J. J. Hurly, Int. J. Thermophys., 2004, 25, 625.
- 7. A. F. Estrada-Alexanders and J. J. Hurly, J. Chem. Thermodyn., 2008, 40, 193.
- G. Kirchhoff, Ann. Phys. Chem., 1868, 134, 177; English translation in Benchmark Papers in Acoustics: Physical Acoustics, ed. R. B. Lindsay, Dowden, Hutchinson & Ross, Stroudsburg, Pennsylvania, 1974, p. 7.
- 9. I. B. Crandall, *Theory of Vibrating Systems and Sound*, Van Nostrand, New York, 1927, 229–241.
- 10. F. B. Daniels, J. Acoust. Soc. Am., 1947, 19, 569.
- 11. J. B. Mehl, J. Acoust. Soc. Am., 1999, 106, 73.
- 12. J. J. Hurly and M. R. Moldover, private communication.
- 13. J. J. Hurly and M. R. Moldover, *J. Res. Natl. Inst. Stand. Technol.*, 2000, **105**, 667.
- 14. J. Kestin and J. Yata, J. Chem. Phys., 1968, 49, 4780.

- 15. E. F. May, R. F. Berg and M. R. Moldover, *Int. J. Thermophysics*, 2007, 28, 1085.
- 16. K. A. Gillis, Metrologia, 2012, 49, L21.
- M. R. Moldover, K. A Gillis, J. J. Hurly, J. B. Mehl and J. Wilhelm, *Modern Acoustical Techniques for the Measurement of Mechanical Properties*, ed. Moises Levy and Henry E. Bass, Academic Press, San Diego, California, USA, 2001, ch. 10, 377–427.
- P. Malbrunot, A. Boyer, E. Charles and H. Abachi, *Phys. Rev. A*, 1983, 27, 1523.
- 19. K. A. Gillis, I. I. Shinder and M. R. Moldover, *Phys. Rev. E*, 2004, 70, 021201.
- 20. K. A. Gillis, I. I. Shinder and M. R. Moldover, *Phys. Rev. E*, 2005, 72, 051201.
- 21. K. A. Gillis, I. I. Shinder and M. R. Moldover, *Phys. Rev.Lett.*, 2006, 97, 104502.
- 22. P. E. Mueller, D. Eden, C. W. Garland and R. C. Williamson, *Phys. Rev. A*, 1972, **6**, 2272.
- 23. J. Thoen and C. W. Garland, Phys. Rev. A, 1974, 10, 1311.