Correlations among acoustic measurements of the Boltzmann constant

CORRELATIONS AMONG ACOUSTIC MEASUREMENTS OF THE BOLTZMANN CONSTANT

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Abstract

We review correlated uncertainties among the accurate determinations of the Boltzmann constant k_B that used the techniques of primary acoustic gas thermometry (AGT). We consider uncertainty contributions from four sources: (1) resonator-dependent uncertainties of the acoustic and microwave measurements, (2), gas-dependent uncertainties from the uncertain chemical and isotopic compositions of the test gases, (3), literature data for the gas properties, and (4), approximations in the theory of AGT. Resonator-dependent uncertainties are correlated when the same cavity was used for more than one measurement. Gas-dependent uncertainties are correlated among those measurements that used argon with isotopic abundances determined using an isotopic standard prepared at KRISS in 2006. All the AGT measurements have small correlated uncertainties from their use of literature data for the Avogadro constant, and for the thermal conductivity and the higher acoustic virial coefficients of helium or argon.

1. Introduction

In 2018, the International System of Units (SI) will be revised. After the revision, the unit of thermodynamic temperature will continue to be the kelvin; however, its magnitude will be set by fixing the numerical value of the Boltzmann constant k_B to be exactly 1.3806X $\times 10^{-23}$ J K^{-1}. The Committee on Data for Science and Technology (CODATA) will determine the digits X using an uncertainty-weighted average of the measured values of k_B that are accepted for publication on or before July 1, 2017. [1] CODATA's determination of X will ensure that accurate measurements of the temperature of the triple point of water T_{TPW} made after the 2018 redefinition will be very close to the presently defined value $T_{TPW} \equiv 273.16$ K, even though the new definition of the kelvin makes no reference to T_{TPW}.

In preparation for the 2018 redefinition of the kelvin, many laboratories have measured k_B using diverse methods. [2] At the time of this writing, several measurements of k_B with the smallest claimed uncertainties have used acoustic gas thermometry (AGT). For these low-uncertainty AGT measurements of k_B, this paper looks for correlations among the contributions to the uncertainty budgets. This search for correlations is also a preparatory step for the 2018 redefinition of the kelvin because CODATA will account for such correlations when it determines the defined value of k_B using an uncertainty-weighted average of the AGT results and the results obtained with other techniques. We encourage feedback that will improve a future version of this search for correlations that is likely to occur soon after CODATA's July 1, 2017 deadline for new measurements.

Table 1 lists the AGT measurements considered here. We identify the selected AGT measurements with the initials of the laboratory of the first author and by the year of publication. The laboratories are: National Institute of Standards and Technology (NIST-88), [3]; Laboratoire Commun de Métrologie (LNE-09) [4]; National Physical Laboratory (NPL-10), [5]; LNE-11 [6]; National Institute of Metrology (NIM-13), [7]; NPL-13, [8]; LNE-15, [9]; and Istituto Nazionale di Ricerca Metrologica (INRiM-15) [10]. (Note: INRiM-15 became available too late to be included in the CODATA-2014 evaluation of k_B.) For completeness, we mention several AGT measurements of k_B that are not included in Table 1. These are NIM-11

[11] which has been superseded by NIM-13, INRiM-10 [12] which has been superseded by INRiM-15, and NPL-79 [13] which has been superseded by NPL-10 and NPL-13.

For each measurement in Table 1, Row 2 is a reference to the initial publication and Row 3 is the determined value of k_B and its relative standard uncertainty[1] $u_r(k_B)$. The standard uncertainties are expressed as deviations from the CODATA-2014 value of k_B using the definition $\Delta k_B \equiv (k_B/k_{B,CODATA\text{-}2014} - 1)$ where $k_{B,CODATA\text{-}2014} = 1.38064852\times(1 \pm 5.7\times10^{-7})\times10^{-23}$ J K^{-1}. [14]

Table 1. Selected AGT measurements of k_B and their correlated uncertainty components. We define $\Delta k_B \equiv (k_B/k_{B,CODATA\text{-}2014} - 1)$ using $k_{B,CODATA\text{-}2014}$ from [14].

Row		NIST-88	LNE-09	NPL-10	LNE-11	NIM-13	NPL-13	LNE-15	INRiM-15
1	Reference	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]
2	Gas	Ar	He	Ar	Ar	Ar	Ar	He	He
3	$10^6[\Delta k_B \pm u_r(k_B)]$	1.19±1.77	0.87±2.73	0.95±3.19	–0.57±1.41	–0.59±3.70	–0.65±0.90	0.21±1.01	1.75±1.06
				Correlated relative uncertainty components, ppm					
	MASS								
4	Molar mass Ar - IRMM			0.70	0.70				
5	Molar mass Ar - KRISS					0.52	0.52		
	TEMPERATURE								
6	TPW - LNE		0.16		0.16			0.16	
	DIMENSIONS								
7	3rd order micro. eigenv.		0.05	0.05	0.05		0.05	0.05	
8	microwave antennas		0.10	0.10	0.10		0.10	0.10	0.10
9	Resonator Volume				0.57			0.57	
	ACOUSTIC ISOTHERM								
10	fitting routine – NPL			0.02			0.02		
11	thermal cond. Ar	0.02		0.02	0.02	0.1	0.02		
12	thermal cond. He		0.02					0.02	0.02
13	3rd order acoust. eigenv.		0.05	0.05	0.05		0.05	0.05	
14	$A_{3,Ar}$ or $A_{2,He}$ coefficients	0.07	0.04	0.05	0.07	0.07	0.08	0.04	0.04

[1] Unless stated otherwise, all uncertainties are standard uncertainties corresponding to a 68 % confidence level.

After consulting with the lead authors, CODATA applied corrections to some of the published values of k_B and their uncertainties to account for improvements in the literature values of the Avogadro constant $N_A = 6.022140857\times(1 \pm 1.2\times10^{-8}) \times10^{23}$ mol^{-1} [14] and of the thermal conductivities of helium [15] and argon (supplementary material in [16]) that became available after the original AGT publications. The values of k_B from NIM-13 and NPL-13 were also corrected for new values of the average molar mass M of the argon. [17, 18]

2. Acoustic Gas Thermometry and the Boltzmann Constant

Here, we outline the connection between acoustic gas thermometry and the Boltzmann constant in enough detail to understand the correlations in the uncertainty budgets. Many additional details and references can be found in Ref. [16]. For AGT, it is convenient to separate the uncertainty budgets into four contributions that result from measurements of (1) the average molar mass $\langle M \rangle$ of the test gas, (2) the thermodynamic temperature T, (3) a key dimension D of a gas-filled acoustic cavity resonator (either an average radius $\langle a \rangle$ or an average length $\langle L \rangle$) and (4) correcting and fitting the pressure-dependence of acoustic resonance frequencies on an isotherm.

2.1 Average molar mass

The Boltzmann constant k_B relates the thermodynamic temperature T to the average energy in a single, statistical-mechanical, degree of freedom. A molecule of mass m has 3 translational degrees of freedom. When such a molecule is in equilibrium with a heat bath, its average kinetic energy $\langle$K.E.$\rangle$ is related to the thermodynamic temperature by: $\langle \text{K.E.} \rangle = (1/2)mv_{RMS}^2 = (3/2)k_BT$, where v_{RMS} is the root-mean-square velocity of a molecule. In an ideal gas of such molecules, v_{RMS} is connected to the zero-frequency speed of sound u_0 and the zero-density heat-capacity ratio $C_p^0/C_v^0 \equiv \gamma_0$ of the gas through $v_{RMS}^2 = (3/\gamma_0)u_0^2$. For an ideal monatomic gas γ_0 is exactly 5/3 and k_B can be obtained using the relation:

$$u_0^2 = \frac{5k_BT}{3m} = \frac{5N_Ak_BT}{3M} = \frac{5RT}{3M} \quad , \tag{1}$$

where u_0^2 is determined by AGT. In the present SI, the mass m of atom is related to the kilogram using the Avogadro constant $N_A = M/m$, where M is the molar mass of gas. Thus, a measurement of u_0^2 using AGT actually determines the universal gas constant $R \equiv k_B N_A$, as indicated by the last equality in Eq. (1). Therefore, all AGT determinations of k_B have a correlated uncertainty contribution from the uncertainty of N_A. According to CODATA-2014, the relative standard uncertainty of N_A is 1.2×10^{-8}, which is only $1/75^{th}$ of the smallest uncertainty AGT value of k_B in Table 1. [14] This correlated uncertainty component of M is so small that we neglect it in this work.

As indicated in Table 1, both argon and helium have been used for the AGT determinations of k_B. First, we consider the argon-based measurements. Commercially-prepared, highly-purified, argon is a mixture of isotopes with approximate mole fractions: $x_{36Ar} = 0.0033$; $x_{38Ar} = 0.0006$; $x_{40Ar} = 0.9961$. For such gases, Yang *et al*. showed that the average molecular mass $\langle M_{Ar} \rangle$ varies by approximately $2\times10^{-6}\ \langle M_{Ar} \rangle$. [17] Thus, $\langle M_{Ar} \rangle$ must be measured for the specific argon samples used during accurate argon-based, AGT determinations of k_B.

NIM-13 used a value of $\langle M_{Ar} \rangle$ that was determined by mass spectroscopy conducted in China. [7] However, the mass spectroscopy used a gravimetrically-prepared argon isotope standard that had been prepared at the Korea Research Institute of Standards and Science (KRISS) [17]. Originally, NPL-13 used a value of $\langle M_{Ar} \rangle$ determined by mass spectroscopy conducted at Institute for Reference Materials and Measurements (IRMM). After reviewing the work of Yang *et al*. [17], NPL-13 revised its result for k_B using the value of $\langle M_{Ar} \rangle$ determined at KRISS using KRISS's gravimetrically-prepared argon isotope standards. [18] Thus, KRISS's argon isotope standard contributed an uncertainty of 0.39 ppm to both the NIM-13 and NPL-13 measurements of k_B. (We define "1 ppm" as 1 part in 10^6.) In addition, KRISS's mass spectroscopy has an incompletely-understood, offset in the mole fraction ratio x_{38Ar}/x_{36Ar} that leads to a 0.35 ppm uncertainty in its determinations of $\langle M_{Ar} \rangle$. The sum in quadrature of 0.39 ppm and 0.35 ppm is the correlated uncertainty of the KRISS values of $\langle M_{Ar} \rangle$ used by NIM-13 and NPL-13 (Table 1, Row 6).

In the original publications, both NPL-10 and LNE-11 used values of $\langle M_{Ar} \rangle$ determined by mass spectroscopy at IRMM. After reviewing the work of Yang *et al*. [17], the uncertainties

of these values of $\langle M_{Ar} \rangle$ were increased to 0.70 ppm (which is the uncertainty of the KRISS values of $\langle M_{Ar} \rangle$) and assumed to be correlated. (Table 1, Row 4)

NIST-88 obtained $\langle M_{Ar} \rangle$ by comparing the speed of sound in their "working gas" with the speed of sound in isotopically enriched ^{40}Ar. The NIST-88 value of $\langle M_{Ar} \rangle$ and its uncertainty are not correlated with the other values $\langle M_{Ar} \rangle$ in Table 1.

Helium has two stable isotopes: ^{3}He and ^{4}He. Most of the helium in commerce is produced from natural gas in the United States of America (USA). Using samples taken from 12 natural gas wells in the USA, Aldrich and Nier [19] measured ^{3}He/^{4}He abundance ratios spanning the range 0.05 ppm to 0.5 ppm. From these results, the naturally occurring ^{3}He in ^{4}He is expected to reduce $\langle M_{He} \rangle$ by 0.012 ppm to 0.12 ppm from M_{4He}. The two gas analyses reported in INRiM-15 are consistent with this expectation. In contrast, speed-of-sound ratios reported in LNE-15 imply that the values of $\langle M_{He} \rangle$ for two different, commercially-produced, highly-purified, helium samples differed by the surprisingly large value 0.44 ppm. LNE-15 accounted for this observation by including an uncertainty component of 0.5 ppm in their error budget. Furthermore, LNE-15 suggested that the two different values of $\langle M_{He} \rangle$ could have resulted from two different concentrations of ^{3}He in ^{4}He. (Note: certain natural gases in Taiwan have ^{3}He/^{4}He abundance ratios as large as 3.8 ppm. [20])

If LNE-15's suggestion of high ^{3}He concentration in commercial ^{4}He is confirmed, the uncertainty of $\langle M_{He} \rangle$ in LNE-09 must be increased and future helium-based, low-uncertainty determinations of k_B must measure the ^{3}He concentration in the samples of helium used for AGT. We are unaware of any correlation among the values of $\langle M_{He} \rangle$ used in LNE-09, LNE-15, and INRiM-15.

2.2 Temperature

Equation (1) contains the thermodynamic temperature T which, in current SI units, is exactly 273.16 K at T_{TPW}. At temperatures only 20 K away from T_{TPW}, the most accurate measurements of T have uncertainties of 0.4 mK (at 290 K) and 0.9 mK (at 255 K) which correspond to 1.3 ppm and 3.5 ppm of T, respectively. [21] To circumvent these comparatively

large uncertainties, all of the AGT measurements listed in Table 1 were conducted within 0.1 K of T_{TPW}.

Each of the AGT determinations of k_{B} discussed here determined the average temperature of the gas inside its cavity resonator from the readings of several capsule-type standard platinum resistance thermometers (SPRTs) that were in good thermal contact with the walls of the cavity. All of the thermometers were calibrated using ITS-90; however, they were used so close to the calibration point T_{TPW} that the uncertainties of ITS-90 were irrelevant (including the uncertainty of the derivative dT_{90}/dT and the uncertain of the discontinuity in dT_{90}/dT at T_{TPW}). The calibrations were conducted both before and after the acoustic measurements; therefore, the dominant uncertainty in the measurement of the temperature came from the random drift of the ratios of the thermometers' resistances to the resistance of a thermostatted, standard resistor. Because the thermometer drifts are random, the uncertainties from the drifts were uncorrelated.

The temperature calibrations for LNE-09, LNE-11, and LNE-15 used the same triple-point-of-water cell, which, in turn was linked to the National Temperature Reference cells of France. The estimated, correlated uncertainty of k_{B} associated with the triple point of water cell is 0.16 ppm. Each of the other AGT determinations of k_{B} used triple-point-of-water cells that were traceable to their National Temperature References. When these National Temperature References were compared in CCT-K7, their values of T_{TPW} spanned a range of 99 μK and had a standard deviation from their mean of 45 μK. [22] Therefore 45 μK, which corresponds to $1.6\times10^{-7}\ T_{\mathrm{TPW}}$, is an estimate of the lowest possible uncertainty of any determination of k_{B} by these laboratories in the year 2006. Subsequent, smaller, inter-laboratory comparisons of T_{TPW} cells have much lower uncertainties. [23]

2.3 Key dimensions

Each of the AGT measurements listed in Table 1 determined the speed of sound (in either helium or argon) as a function of the pressure p on the isotherm T_{TPW} using the equation

$$u(p,T_{\mathrm{TPW}}) = D\left[\, f_{\mathrm{a}}(p) - \Delta f_{\mathrm{a}}(p)\right] / z_{\mathrm{a}}^{*} \quad . \qquad (2)$$

Here, $f_a(p)$ are the real parts of the measured values of the complex acoustic resonance frequencies of selected modes of a gas-filled cavity, D is a key dimension of the cavity, z_a^* is a calculated acoustic eigenvalue (that depends on the mode and the shape of the cavity), and $\Delta f_a(p)$ are calculated corrections to the measured resonance frequencies. (Note: the eigenvalues denoted "z_a^*" differ from the conventionally defined eigenvalues by a cavity-shape-dependent numerical factor.) The values of the calculated corrections $\Delta f_a(p)$ depend on properties of the apparatus (size and shape of the cavity, surface finish and elastic recoil of the cavity's walls, ducts, microphones, *etc*.), the properties of the gas (thermal conductivity, viscosity) and the gas-wall interaction (thermal and viscous accommodation coefficients).

The shapes of the cavities and the symmetry of the selected acoustic modes (cylinder and longitudinal modes; sphere or quasi-sphere and radially-symmetric modes) were chosen for two reasons: (1) small imperfections in the shape of the cavity of size $D\varepsilon$ generate very small corrections to the eigenvalues on the order of $z_a\varepsilon^2$ and (2) the selected modes are non-degenerate so that their center frequencies could be determined within a very small fraction of the half-width of the modes.

In NIST-88, the cavity was nearly spherical; the key dimension was $D = \langle a \rangle$ the average radius of the cavity and the frequencies $f_a(p)$ of the radially-symmetric acoustic modes were measured. NIST-88 determined $\langle a \rangle$ by weighing the mercury required to fill the cavity using literature values for the density of mercury. In NIM-13, the cavity was nearly a right circular cylinder; the key dimension was $D = \langle L \rangle$ the average length of the cavity, and the frequencies $f_a(p)$ of the longitudinal symmetric acoustic modes were measured. NIM-13 determined $\langle L \rangle$ *in situ* using two-color optical interferometry. The determinations of $\langle a \rangle$ by NIST-88 and $\langle L \rangle$ by NIM-13 are uncorrelated with the other determinations of D.

Each of the 6 other determinations of k_B in Table 1 determined u from measurements of the frequencies $f_a(p)$ of the radially-symmetric acoustic modes of a quasi-spherical cavity. Except for INRiM-15, the cavities were designed to be tri-axial ellipsoids with axes in the ratio a:$a(1+e_1)$:$a(1+e_2)$ where typical values are a = 50 mm to 90 mm, $e_1 = 0.0005$ and $e_2 = 0.0010$. The values of a, e_1 and e_2 were determined from measurements of the frequencies of the microwave modes of the cavity. To facilitate the microwave measurements, the cavities were designed so that e_1 and e_2 were large enough to separate the triply-degenerate microwave

resonances of a perfectly spherical cavity into three, fully-resolved resonances. However, the values of e_1 and e_2 were not so large that they significantly modified the radially-symmetric acoustic modes. The key dimension needed to determine the speed of sound is the average radius of a spherical cavity with the same volume as the quasi-sphere $D = a[(1+e_1)(1+e_2)]^{1/3}$. This dimension and the values of e_1 and e_2 were determined at the pressures p and T_{TPW} by fitting the measured microwave frequencies $f_m(p)$ using

$$c = Dn(f_m - \Delta f_m)_{p,TPW} / z_m^* \quad . \qquad (3)$$

In Eq. (3), c is the speed of light in vacuum, n is the refractive index of the gas at the microwave frequencies at p and T_{TPW}, Δf_m are corrections to the measured frequencies that we discuss below, and z_a^* is a calculated microwave eigenvalue (that depends on the mode and e_1 and e_2). (Note: the eigenvalues denoted "z_m*" differ from the conventionally defined eigenvalues by known numerical factors.)

The electromagnetic eigenvalues z_m* [24] and acoustic eigenvalues z_a* [25] of a triaxial ellipsoidal cavity have been calculated analytically to 2nd order in the small quantities e_1 and e_2. A numerical calculation of the 3rd-order contributions to z_m* is also available [24]; however, it appears that it was not used by LNE-09, NPL-10, LNE-11, NPL-13, and LNE-15. For the determinations of k_B in Table 1, we estimate the correlated uncertainty from 3rd-order contribution to z_m* is 0.05 ppm. (Table 1, Row 7) The INRiM-15 cavity was assembled from nearly spherical hemispheres that were deliberately misaligned. The microwave spectrum measured by INRiM-15 was well approximated by that of a triaxial ellipsoid with the very small values e_1 = 0.00020 and e_2 = 0.00010; therefore, 3rd-order contributions to z_m* are negligible. [INRiM-15 did not estimate Δf_m and $u(\Delta f_m)$ generated by the step-like shape perturbation at the joint between the hemispheres.].

In Eq. (3), the corrections to the measured microwave frequencies, $\Delta f_m(p)$ account for: (1), the penetration of the microwave fields into the walls of the cavity (2), the microwave antennas and/or waveguides coupling the cavity to coaxial cables, (3) acoustic transducers embedded in the cavity's walls, (4) ducts admitting gas into the cavity, (5) dielectric films (*e.g.* oxides) on the interior surfaces of the cavity, and (6) loading of the cavity by the coaxial cables and the vector analyzer that were used to measure the microwave frequencies. We now consider the correlated uncertainties resulting from the uncertainty of these corrections.

2.3.1 Penetration of microwave fields into the cavity's walls

The microwave fields in a cavity decay within the cavity's wall with an exponential decay length $\delta = (\pi \mu_r \mu_0 \sigma_{cond} f)^{-1/2}$, where μ_r and σ_{cond} are the relative magnetic permeability and electrical conductivity of the cavity's wall. The same decaying fields increase the half-width g_m of each microwave mode by $g_m = -\Delta f_m$. The correction Δf_m is significant; for NPL-13 it ranges from 4 ppm to 16 ppm of f_m, which is equivalent to 8 ppm to 32 ppm of k_B. After external contributions to the half-widths are taken into account, $g_m = -\Delta f_m$ and the easily measured half-widths g_m can and are used to estimate Δf_m and σ_{cond} at the microwave frequencies of interest. (For this purpose, Underwood *et al.* [26] have argued that microwave modes that generate currents which cross the joint between the quasi-hemispheres should be excluded; however, this exclusion was insignificant for INRiM-15.) When Δf_m is estimated from measured values of g_m, the relative uncertainty $u_r(D)$ is inferred from the scatter of the values of D deduced from 10 or so microwave modes. The scatter in the various measurements does not have obvious correlations. Typically, $u_r(D) < \sim 10^{-7}$ which corresponds to $u_r(k_B) < \sim 2 \times 10^{-7}$.

In every case, the measured values of g_m exceed the values of $g_{m,calc}$ that are calculated using the low-frequency value of $\sigma_{cond,DC}$. In recent measurements (LNE-11, NPL-13, INRiM-15), the ratio $(g_{m,meas} - g_{m,calc})/g_m$ ranges from 0.01 to 0.04 and it tends to increase with frequency. This tendency has been observed at higher frequencies, even after strenuous efforts were made to minimize surface roughness and work hardening. [27] Thus, one must consider the possibility that the frequency-dependence of the surface conductivity of copper is not understood, within the uncertainty of the present measurement of g_m.

2.3.2 Microwave antennas and waveguides

Underwood *et al.* calculated Δf_m for straight antennas and ducts (waveguides). [28] By using comparison measurements, LNE-11 showed that straight antennas and loop antennas yield values of D that differed by only 0.054 ppm of D, thus, Δf_m for loop antennas is linked to Δf_m for straight antennas. We estimate $u(\Delta f_m)$ is on the order of 5 % to 6 % of the calculated perturbation and it contributes a uncertainty $u(k_B)$ = 0.10 ppm that is correlated among the

measurements that used [28]. (Table 1, Row 8) At the time LNE-09 was conducted, the effects of antennas had not been fully quantified; therefore, LNE-09's value of k_B (and its associated uncertainty) should be updated to account for the antennas. However the update would change k_B much less than its uncertainty.

2.3.3 Microwave effects of acoustic transducers

Except for NIM-13, each AGT determination of k_B used two, similar, capacitive microphones embedded in the wall of the cavity such that the diaphragm of each microphone was approximately flush with the interior surface of the cavity. The AGT experiments used diverse means to quantify "approximately flush." They included: microscopic observations (NPL-13 and INRiM-15), using a soft compound to make and measure replicas of the cavity's surface including the installed microphone (NPL-13), and measuring the changes in f_m that occurred upon replacing copper plugs with the microphones (NPL-10, LNE-11, NPL-13, INRiM-15). Each microphone's protrusion into (or the recess from) the wall of its cavity depended on apparatus-specific details; therefore, the associated uncertainty was not correlated with the corresponding uncertainty from the other AGT measurements of k_B.

The microphones' diaphragms had a lower electrical conductivity than that of the surrounding copper and that an annular groove separated each diaphragm from the surrounding copper. When NPL-10 replaced copper plugs with microphones, the scaled half-width of two components of the TM11 triplet increased approximately 0.8 ppm; these components had high current densities at the microphones. The third component of the TM11 triplet and the components of the TM12 mode did not increase. The effect of the diaphragms' conductivity on f_m is taken into account when the half-widths gm are used to account for the penetration of the microwave fields into the cavity's wall.

2.3.4 Other microwave perturbations

The contributions to $u(k_B)$ from the ducts admitting gas into the cavity, possible dielectric films on the interior surfaces of the cavity, and the loading of the cavity by the coaxial cables and the vector analyzer depend upon specific details of each apparatus (e.g. the lengths and diameters of

the ducts, the surface and history of the cavity, etc.); therefore, uncertainties from these sources are uncorrelated.

LNE-11 and LNE-15 both used the same cavity resonator to determine k_B. The Type B uncertainties of the microwave determinations of the average radius of this cavity were far larger than the Type A uncertainties. (See Fig. 6 of LNE-15) Therefore, the uncertainty of $u(D)$ is completely correlated between these two measurements. (Table 1, Row 9)

2.4 Correcting and fitting acoustic resonance frequencies on the isotherm T_{TPW}

The thermodynamic speed of sound (*i.e.* the speed of sound at zero frequency) and at zero pressure cannot be measured. For the monatomic gases, the frequency-dependencies of the speed of sound are known and are too small to be considered here. [29] AGT determinations of k_B measure $u(p,T_{TPW})$ as a function of the pressure p and rely on the exact virial expansion:

$$u^2(p,T_{TPW}) = u_0^2 + \sum_{i=1} A_i(T_{TPW})\, p^i \qquad (4)$$

to determine u_0. Exact thermodynamic relationships connect the acoustic virial coefficients $A_1(T)$, $A_2(T)$, . . . to the density virial coefficients and their temperature derivatives [30, 31].

For AGT determinations of k_B, the speed of sound $u(p,T_{TPW})$ is determined by measuring the frequencies of the acoustic resonances $f_a(p,T_{TPW})$ using

$$u(p,T_{TPW}) = D(f_a - \Delta f_a)_{p,TPW} / z_a^* \quad . \qquad (5)$$

Here, $\Delta f_a(p,T_{TPW})$ are corrections to f_a that we will discuss below. When Eqs. (4) and (5) are combined, we get a polynomial equation in which kB is one of many parameters.

$$\left[D\,(f_a - \Delta f_a)_{p,TPW} / z_a^* \right]^2 = \frac{5k_B N_A T_{TPW}}{3M} + \sum_{i=1} A_i(T_{TPW})\, p^i \quad . \qquad (6)$$

We emphasize that Eq. (5) is always applied to measurements made using several different acoustic modes at each pressure. Each mode determines a value of k_B; therefore, the use of several modes generates redundant data. This redundancy facilitates very precise tests of the theories for the frequency corrections Δf_a,and for the eigenvalues z_a^*. Indeed, redundancy distinguishes AGT from other forms of gas thermometry.

As for the microwave eigenvalues, the acoustic eigenvalues z_a* of a triaxial ellipsoidal cavity have been calculated analytically to 2nd order in the small quantities e_1 and e_2. [25] Also, a numerical, 3rd-order calculation of z_a* is available; however, it appears that it was not used to model the cavities in LNE-09, NPL-10, LNE-11, NPL-13, and LNE-15. For the determinations of k_B in Table 1, we estimate the correlated uncertainty from neglect of the 3rd-order calculation of z_a* is 0.05 ppm. (Table 1, Row 13) For the INRiM-15 cavity, the values of e_1 and e_2 were so small that the 3rd -order contribution to z_a* was negligible.

The pressure-dependence of the acoustic resonance frequencies is more complicated than the pressure-dependence of the speed of sound itself because of the corrections Δf_a to the measured acoustic frequencies. First, we consider gas-dependent corrections, which are correlated among the various AGT measurements of k_B because they rely on the best values of the gas' properties taken from the same sources. Then, we consider apparatus-dependent corrections, which are uncorrelated among the various AGT measurements. We note that the same cavity was used for LNE-13 and LNE-15; however, when the cavity was filled with helium, the acoustic resonance frequencies were 3.2 times larger than when the cavity was filled with argon. Therefore, there is no correlation of the important, apparatus-dependent, recoil correction between LNE-13 and LNE-15.

2.4.1 Thermal boundary layer

Throughout the volume of the gas-filled cavity, temperature oscillations at frequency f_a accompany the acoustic pressure oscillations. The temperature oscillations decay with an exponential decay length $\delta_T = [\lambda/(\rho C_p \pi f_a)]^{1/2}$ on the gas side of the boundary between the gas and the cavity's wall. Here λ is the thermal conductivity of the gas, ρ is its mass density, Cp/M is the constant-pressure molar heat capacity (which is exactly 5R/2 for monatomic gases in the limit of zero density) and M is the average molar mass. For the radially symmetric acoustic modes of a spherical or quasi-spherical cavity with radius a, the decay of the temperature oscillations generates contributions to the real and the imaginary (half-width) parts of the resonance frequencies given by

$$\frac{\Delta f_{\text{therm}} + i g_{\text{therm}}}{f_{\text{a,0}}} = \left((-1+i)(\gamma-1)\frac{\delta_{\text{T}}}{2a} - i(\gamma-1)(4\gamma-2)\left(\frac{\delta_{\text{T}}}{2a}\right)^2 \right)\left[1 - \frac{(\delta_{\text{T}}\lambda)_{\text{shell}}}{(\delta_{\text{T}}\lambda)_{\text{gas}}} \right] , \qquad (7)$$

where $f_{\text{a,0}}$ is the unperturbed acoustic resonance frequency and the term in square brackets accounts for temperature oscillations in the cavity's wall. [32] In the optimum pressure range for AGT determining k_{B} (argon: 100 < p/kPa < 500; helium: 300 < p/kPa < 900), typical values of $\Delta f_{\text{therm}}/f_{\text{a,0}}$ range from the equivalent of 100 ppm to 400 ppm of k_{B}. [16] Thus Δf_{therm} is the largest correction to simple models of AGT and it requires accurate values of λ, ρ, and C_{p}. This requirement stimulated Cencek *et al*. to conduct accurate, *ab initio*, calculations of λ, ρ, and C_{p} for helium. [15] The resulting values of λ, ρ, and C_{p} were used by LNE-15 and by INRiM-15 and also in CODATA-2014's reanalysis of LNE-09. The uncertainty of the calculated values of λ, ρ, and C_{p} are propagate into the correlated uncertainty of k_{B} listed in Table 1, Row 12. Within their noise, measurements of g_{therm} confirm the accuracy of Eq. (12) in the limit of low pressures for several radial acoustic modes of several resonators. (See, for example, INRiM-15, NPL-13, and LNE-15.) We emphasize that this confirmation has no adjustable parameters.

As of this writing, the most accurate values of λ, ρ, and C_{p} for argon and their uncertainties are available only in the Supplementary Material of [16]. These values are based on a recently-calculated, *ab initio* argon-argon interatomic potential that has been slightly adjusted to be consistent with accurate measurements of the viscosity ratio $\eta_{\text{Ar}}/\eta_{\text{He}}$ and with measurements of the second acoustic virial coefficient of argon. The values of k_{B} in NIST-88, NPL-10 and NPL-13 were recalculated using these recent values of λ, ρ, and C_{p}. The corresponding correlated uncertainty of k_{B} listed in Table 1, Row 12.

2.4.2 Viscous boundary layer

The velocity of acoustic oscillations of the longitudinal modes of the cylindrical cavity used by NIM-13 is parallel to the side wall of the cavity. This velocity decays exponentially to zero at the boundary between the gas and the wall with the characteristic decay length $\delta_{\text{v}} = [\eta/(\rho\pi f)]^{1/2}$. As discussed in detail in NIM-13 and near Eq. (9) of [16], both the shear viscosity η_{Ar} and the thermal conductivity λ_{Ar} generate frequency corrections and half-width contributions that are

approximately 5 times larger than the corresponding corrections for a spherical or quasi-spherical cavity of equal volume and with a length equal to its diameter. Thus, we estimate that NIM-13 has the correlated uncertainty of 0.1 ppm of k_B from the uncertainties of the calculated values of η, λ, ρ, C_p for argon. (Table 1, Row 11)

2.4.3 Acoustic virial coefficients

In Eq, (4), the acoustic virial expansion of $u^2(p,T_{TPW})$ for helium, $A_{2,He}p^2$ is the highest-order term that contributes at least 1 ppm to $u^2(p,T_{TPW})$; for argon, the highest-order contributor is $A_{3,Ar}p^3$. The coefficients $A_{2,He}$ and $A_{3,Ar}$ are more accurate determined, either from *ab initio* calculations, or from speed-of-sound measurements at high pressures than from multi-parameter fitting of Eq. (6) to AGT data. Thus, for helium, Eq. (6) is rewritten in the form

$$\left[D \left(f_a - \Delta f_a \right)_{p,TPW} / z_a^* \right]^2 - A_2(T_{TPW})\, p^2 = \frac{5 k_B N_A T_{TPW}}{3M} + A_1(T_{TPW})\, p \quad . \qquad (8)$$

After this is done, only two parameters remain on the right-hand side to be fitted to the data for each mode on the left-hand side. However, the uncertainty of $A_{2,He}$ is common to all the helium-based AGT determinations of k_B. The result of propagating $u(A_{2,He})$ taken from the *ab initio* calculation of [33] appears in Table 1, Row 14 for INRiM-15, LNE-15, and LNE-09.

For argon, the term $A_{3,Ar}(T_{TPW})p^3$ is moved to the left hand side of an equation analogous to Eq. (8). The result of propagating $u(A_{3,Ar})$ taken from either [34] or [35] appears in Table 1, Row 14 for all the argon-based AGT measurements of k_B.

2.4.4. Uncorrelated, apparatus-dependent uncertainties.

We briefly consider two apparatus-dependent sources of uncertainty, which we believe are uncorrelated. They are: (1) the recoil of a cavity wall's in response to the oscillating acoustic pressure, which generates acoustic frequency corrections Δf_a that grow approximately as the static pressure p with a slope that has a complicated frequency dependence and, (2) the thermal accommodation coefficient, which generates acoustic frequency correction Δf_a of the form $A_{-1}(p)^{-1}$. An analogous momentum accommodation coefficient applies only to NIM-13;

therefore it does not generate correlated uncertainties even though it has the functional form form $\Delta f_a \propto A_{-1}(p)^{-1}$.

Following [16], we consider only the simplest model for the recoil of the shell enclosing a cavity filled with a gas near an acoustic resonance of the gas. When the gas resonance is not too close to a resonance of the empty shell, the theory predicts that the frequency of the gas resonance is shifted by

$$\frac{(\Delta f_l)_{\text{shell},i}}{f_l} \approx -\left(\rho u^2\right)_{\text{gas}} \frac{G_{i,l}}{1-\left(f_l / f_{\text{shell},i}\right)^2} \quad , \qquad (9)$$

where the subscript l represents the indices of a gas mode, the subscript i represents the indices of a shell mode, and $G_{i,l}$ is a compliance that depends upon the geometry and elastic properties of the shell and the symmetry of the gas mode l,. In the density range spanned by AGT, $(\rho u^2)_{\text{gas}}$ is nearly proportional to the pressure and $f_l/f_{\text{shell,i}}$ varies only a few percent. Therefore, the perturbations $(\Delta f_l)_{\text{shell,i}}$ are nearly linear functions of the pressure, unless $f_l \approx f_{\text{shell,i}}$ (that is, the resonance frequencies of the gas and the shell nearly coincide..

NIST-88 applied the recoil correction Eq. (8) using only one mode of the shell (the radially-symmetric breathing mode) coupling to five radially-symmetric modes of the gas. For the breathing mode, the NIST-88 values of $G_{\text{breathing}}$ of $f_{\text{breathing}}$ in Eq. (8) were consistent with values that they obtained from independent, non-acoustic measurements. After applying the 2-parameter correction in the form of Eq. (8), NIST-88 determined a single value of A_1 in Eq. (6) using data from 5 acoustic modes. However, the shells used for subsequent AGT determinations of k_B had much more complex recoil behavior. (See especially [36].) The radial acoustic modes of these resonators coupled to a breathing-like mode and many other shell modes. The recoil of such shells might be consistent with a sum of terms in the form of Eq. (8). However, such a sum has too many empirical parameters to be useful. Instead, these determinations of k_B treated A_1 in Eq. (8) as a mode-dependent parameter. (For example, data for 5 modes would generate 5 values of A_1.) When this is done, the multiple values of A_1 are shell-dependent; therefore, they are uncorrelated among the AGT determinations of k_B and they are only approximations of the acoustic virial coefficient in Eq. (6).

For each of the AGT measurements of k_B except NIM-13, two condenser microphones were embedded in the metal wall surrounding the cavity. Each microphone had a diameter of ¼ inch, with the exception of the NPL-13 microphones that had diameters of 1/8 inch. Guianvarc'h *et. al*. carefully modelled the frequency-dependent admittance (both amplitude and phase) of these electro-mechanical systems. [37] In their model, the admittance is approximately a linear function of pressure. For low gas pressures, the model's admittance is nearly constant at low frequencies; however, the admittance has a resonance peak that occurs near the fundamental resonance frequency of the microphone's stretched diaphragm. The model's pressure- and frequency-dependencies are analogous to those of the breathing mode of a spherical shell represented by Eq. (8). Unlike the resonances of a shell, the resonance of the microphone's diaphragm is intentionally damped by gas flows inside the microphone's case. This damping has strong gas-dependencies and pressure-dependencies. The differences between the actual admittance of specific microphones and the model admittance [37] depend upon details of each microphone's construction and history, such as the tension in the diaphragm, the distance between the diaphragm and its back-plate and the dimensions of damping ducts in back-plate. These details are not correlated among different apparatus. Although LNE-11 and LNE-15 used the same microphones, they were used at very different frequencies and had very different gas-dependent damping. Therefore, the microphone-dependent uncertainties in LNE-11 and LNE-15 are uncorrelated.

Kinetic theory predicts that a temperature jump occurs at a gas-solid interface when heat is transferred across the interface. [38] Ewing *et al*. [39] discussed the acoustic consequences of the temperature jump and concluded that the temperature jump increases the resonance frequencies and leaves the resonance half-widths unchanged. The frequency increase is $\Delta f/f = (\gamma - 1)l_a/a$, where l_a is the thermal accommodation length. For a monatomic gas

$$l_a = \frac{\lambda}{p}\sqrt{\frac{\pi m T_{TPW}}{2k_B}}\,\frac{2-h}{2h} \quad , \qquad (10)$$

where h is the thermal accommodation coefficient. (If $h = 1$, l_a equals 1.8 times the mean free path. For argon at T_{TPW}, 100 kPa, and $h = 1$, l_a = 118 nm.) The coefficient h accounts for the fraction of the gas molecules incident on the solid that are reflected or re-emitted from the solid with the kinetic energy expected from the solid's temperature. Thus h might depend upon the

gas, the temperature, and the microscopic conditions of the surface (*e.g.* oxidized or covered with an oil film). We are not aware of systematic acoustic studies of these surface-dependent effects; however, there are numerous, systematic studies of the surface-dependence of steady heat transfer at pressures where the temperature jump is important. For example, Semyonov *et al.* measured the heat transfer from hot wires to helium (and other gases). [40] His results (especially his Fig. 8) show that the heat transfer is sensitive to various cleaning procedures.

The measured acoustic resonance frequencies f_a are corrected for the temperature jump by adding the frequency-independent term $A_{-1}p^{-1}$ to the right hand side of Eq. (8). Therefore, the coefficient A_{-1} is determined when fitting the pressure-dependence of the acoustic frequencies. Because the thermal accommodation coefficient is sensitive to unknown, history-dependent, atomic-scale details of the solid-gas boundary, it is uncorrelated among the AGT determinations of k_B.

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