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► **To cite this version:**

Laurent E Pitre, Mark D. Plimmer, Fernando Sparasci, Marc E. Himbert. Determinations of the Boltzmann constant. *Comptes Rendus. Physique*, 2019, 20, pp.129-139. 10.1016/j.crhy.2018.11.007 . hal-02166573

HAL Id: hal-02166573

<https://hal.science/hal-02166573v1>

Submitted on 28 Jun 2019

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Contents lists available at ScienceDirect

Comptes Rendus Physique

www.sciencedirect.com

The new International System of Units / *Le nouveau Système international d'unités*

Determinations of the Boltzmann constant

Déterminations de la constante de Boltzmann

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ARTICLE INFO

Article history:

Available online 20 December 2018

Keywords:

Boltzmann constant
Primary thermometry
International System of Units (SI)

Mots-clés:

Constante de Boltzmann
Thermométrie primaire
Système international d'unités

ABSTRACT

We review measurements of the Boltzmann constant, k , the value of which is soon to be fixed at exactly $1.380649 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$ for the future revised *Système international* of units. In addition to a description of the theoretical background and of diverse experimental techniques (acoustic thermometry, Johnson noise thermometry, dielectric constant gas thermometry, and Doppler broadened molecular spectroscopy), the article highlights the decisive role of *ab initio* calculations of the thermophysical properties of gases, especially helium-4. Perspectives for improvements in thermometry are outlined in the wake of the new definition.

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R É S U M É

Nous passons en revue des mesures récentes de la constante de Boltzmann, k , dont la valeur sera bientôt figée à $1,380649 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$ dans le cadre du nouveau Système international d'unités. Au-delà d'une description des éléments théoriques et de diverses techniques expérimentales (thermométrie acoustique, thermométrie à bruit de Johnson, thermométrie à constante diélectrique d'un gaz et élargissement Doppler en spectroscopie moléculaire), cet article met l'accent sur le rôle clé des calculs *ab initio* des propriétés thermophysiques des gaz, notamment celles de l'hélium 4. Sont également mentionnées des perspectives pour des améliorations en thermométrie dans le sillage de la nouvelle définition.

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1. Introduction

In 2018, the International System of Units, or *Système international* (SI), will undergo its biggest revolution since the meter–kilogram–second (MKS) system was established with the 1875 *Convention du mètre*. Henceforth, the definitions of all seven base units (meter, second, kilogram, ampere, kelvin, candela, and mole) will be phrased in terms of fixed values

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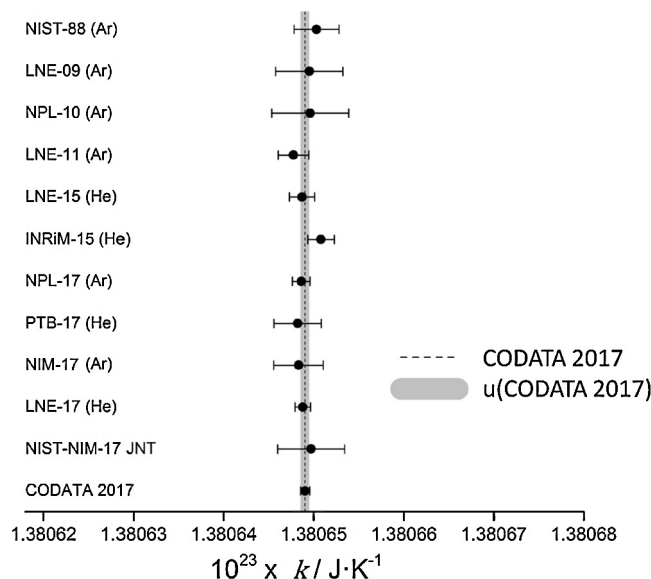


Fig. 1. Measurements of the Boltzmann constant included in the 2017 CODATA adjustment. In the cases of acoustic and dielectric gas thermometry, the gas used is given in parentheses. The measurement NIM-NIST-17 used Johnson noise thermometry JNT. References: NIST-88 [1], LNE-09 [2], NPL-10 [3], LNE-11 [4], LNE-15 [5], INRIM-15 [6], NPL-17 [7], PTB-17 [8], NIM-17 [9], LNE-17 [10], NIST-NIM-17 [11], CODATA 2017 [12].

of a physical constant. In particular, the unit of thermodynamic temperature, the kelvin, will no longer be based on an exact value for the temperature of the triple point of water ($T_{\text{TPW}} = 273.16 \text{ K}$), but rather on a fixed value of the Boltzmann constant k ($1.380649 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$). It has thus been essential that the most accurate and reliable value of k be determined before it is fixed for the foreseeable future. The Consultative Committee for Thermometry (CCT) stipulated that the relative standard uncertainty of the weighted mean of all measurements should be lower than 1×10^{-6} (1 part per million or ppm). Moreover, at least two different methods would have to be used, with at least one result obtained using each method having a relative standard uncertainty better than 3 ppm.

The present article describes how this has been achieved in several different series of experiments by a host of groups worldwide over the past fifteen years or so. Fig. 1 shows the results of the most recent determinations together with the value of the final 2017 CODATA adjustment. In addition to a presentation of the requisite theoretical background for the different experimental thermometry techniques employed (acoustic, dielectric, Johnson noise, Doppler), we highlight the importance of the *ab initio* calculation of the thermophysical properties of gases, particularly of helium-4, without which the current level of accuracy for acoustic and dielectric constant measurements could never have been achieved. Fig. 2 shows how the accuracy of three of the aforementioned methods has improved in recent years. The article is not intended, however, to be an exhaustive list of all the experiments performed. For a more complete overview, the reader is referred to the paper by Fischer et al. [13].

The remainder of the article is structured as follows. In Section 2 we explain the common rationale behind all the determinations of the Boltzmann constant that have achieved the level of accuracy stipulated for the redefinition of the kelvin. Thereafter, in Section 3, we describe the methods that have yielded results used for the CODATA 2017 Special Adjustment of the Fundamental Constants [12] whereby the definitive values of k , the Planck constant h , the fundamental charge e , and the Avogadro constant N_A were ascertained. We shall see that, though apparently diverse, the techniques have several features in common with each other, as well as with methods used to determine other fundamental constants. Indeed, acoustic measurements of k are made on bulk samples where the constant determined is in fact the universal gas constant $R = N_A k$. However, since the relative uncertainty in N_A at the time of measurements (1.2×10^{-8}) [14] was negligible compared with that in k ($\approx 1 \times 10^{-6}$), the accuracies in the determinations of k and R are essentially equivalent. In the revised SI, the value of R will naturally be fixed too. Similarly, in determinations of k by Johnson noise thermometry (JNT), the quantity actually measured is the ratio k/h , the relative uncertainty in h (1.2×10^{-8}) [14] contributing negligibly to that of k . Finally, in Section 4, the implications of a kelvin based on a fixed value of k are outlined, notably as regards prospects for more accurate thermometry over a more continuous, wider range of temperature than with the pre-2018 definition of the unit.

2. Determinations of the Boltzmann constant: rationale

The essential requirement for determining k experimentally is a relation between T_{TPW} and the physical quantities measured. This alone is not enough, however, since one must be able to measure all the experimental parameters with the required level of accuracy. Favorable laws include those relating temperature to the speed of sound and molar mass,

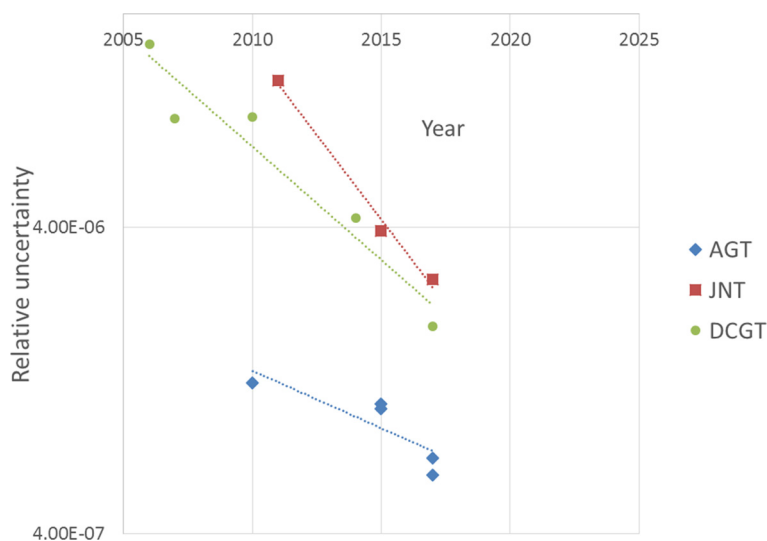


Fig. 2. Progress in the determinations of the Boltzmann constant by three methods: acoustic gas thermometry (AGT), dielectric constant gas thermometry (DCGT), and Johnson noise thermometry (JNT).

the dielectric constant or the refractive index, the electrical noise power in a given bandwidth or the spectral width of an optical absorption resonance. In acoustic thermometry, discussed below, in addition to temperature, it is possible to determine acoustic resonance frequencies, the dimensions of the resonator as well as the molar mass of the acoustic gas, all to better than a part per million. On the other hand, in ideal gas thermometry, based on the ideal gas equation $pV = nRT$, where n is the molar gas concentration per unit volume, it turns out to be impossible to measure n and the volume V at a competitive level of accuracy, especially since the latter includes the volume of connecting tubes to pressure gauges. Other unfavorable laws from an instrumental point of view are, for example, Einstein's law of Brownian motion [15,16] and the Curie law describing the magnetization of a sample [17]. The Planck law for black-body radiation could not be used to measure k at the level of a few ppm either, state-of-the-art radiometric temperature measurements achieving at best 20 to 100 ppm uncertainty [18]. However, a recent review concluded that "blackbody-radiation thermometry, along with acoustic gas thermometry, will be one of the widely accepted methods for thermodynamic temperature measurements based on the new definition of the kelvin" [19].

A second major requirement and challenge is the need to thermalize the gas of molecules or electrons and to measure their temperature. It is for the latter reason that all accurate determinations of the Boltzmann constant have been carried out on samples at temperatures very close to T_{TPW} since it has been the only one measurable with sub part-per-million accuracy with the present, water-based definition of the kelvin.

Finally, in every experiment, the simple equation on which the principle is based must be corrected to allow for several extra effects. It is often as much the uncertainty in the correction terms as that of the terms of the basic equation that limits the accuracy of the method. In acoustic gas thermometry, the dominant correction term is related to the acoustic boundary layer (especially in experiments with helium). The pressure-dependent virial terms can be removed by making measurements at different pressures and extracting the pressure-independent part. For helium and argon, after years of painstaking effort by several groups [20–22], the accuracy of *ab initio* calculations of the lowest-order terms is comparable with and in some cases surpasses that of experiment [23]. The uncertainty in the boundary layer correction has been reduced ten-fold over the past two decades [23,3,24], thanks to improved *ab initio* calculations of the thermal conductivity of helium and argon. In dielectric constant gas thermometry [25], the relative electric permittivity ϵ_r is a function of both pressure and temperature. Here, owing to a necessary hydrostatic correction, the pressure measurement is a limiting factor, aside from dielectric virial corrections and compressibility issues. *Ab initio* calculations of electromagnetic virial coefficients have also benefited acoustic thermometry where, in modern experiments, the resonator's dimensions are measured by electromagnetic resonance. The latter also serves as a cross-check of pressure and temperature measurements and helps spot impurities, the presence of which would alter the result. In Doppler broadening thermometry, the absorption lineshape is not a purely Gaussian profile as a result of collisional broadening (the natural linewidth due to spontaneous emission is usually negligible). For the polyatomic molecular species such as water and ammonia employed for measurements of k , pressure-dependent broadening coefficients cannot be calculated *ab initio*. Moreover, the lineshapes are analyzed using more-or-less sophisticated models, none of which describes perfectly light-matter interaction; the validity of such models is the stumbling block to higher accuracy. In this respect, atomic helium has less-than-ideal properties. Although its collisional broadening coefficients could be calculated with negligible uncertainty, the helium resonance lines lie in the vacuum ultra-violet where there exist as yet no continuous wave laser sources. Even then, aside from fragile cell windows and detectors, photoionization of the excited species would surely complicate lineshape analysis.

3. Experimental measurements of k

In this section, we describe first measurements using acoustic gas thermometry, since ultimately these have provided the most accurate determinations of k . Thereafter, we discuss two other competitive methods, albeit slightly less accurate ones: dielectric constant gas thermometry and Johnson noise thermometry. Finally, we look at Doppler-broadened molecular spectroscopy, an optical route to the value of k that provides a valuable cross-check of the other methods.

3.1. Acoustic gas thermometry

Sound is the propagation of a local density wave in a gas, the speed of which is a function of temperature and pressure [26]. Acoustic gas thermometry relates the speed of sound in a gas of known composition to the thermodynamic temperature [21]. State-of-the-art accuracy requires one to take into account departures from ideal gas behavior. For monatomic gases, where the specific heat capacities at constant volume and pressure are temperature-independent, the acoustic velocity c , extrapolated to zero pressure, is related to temperature T in a simple way:

$$c^2 = (5/3)RT/M \quad (1)$$

where R is the universal gas constant and M the molar mass. Isotopic abundance issues have limited the choice to argon and helium-4, where a single isotope dominates. One advantage of the latter stems from recent high-accuracy *ab initio* calculations of acoustic and dielectric virial coefficients made possible by the relatively simple atomic structure of this dielectronic atom. A second advantage, and one that also motivated its use in the final LNE-CNAM measurement of k is gas purity. By using cold traps at around 5 K, all impurity gases can be removed from helium-4 gas, leaving only trace amounts of helium-3 (0.01 to 1 ppm, depending on the source of the helium). To avoid contamination, a flowing system is used and measurements are performed only once equilibrium has been reached, typically after several tens of hours. At the same time, given the almost negligible amount of helium-3, isotopic abundance is not really an issue. This contrasts with the case of argon, where for a time it was a source of considerable discussion [27].

The most accurate measurements use spherical or quasi-spherical shaped resonators due to the correspondence between the shape of the resonator and the standing wave in the resonator (in this geometry, the radial wave does not interact with any orthogonal angle). To determine the speed of sound in the resonator, one measures the frequencies of several radial acoustic modes. These are related to the speed of sound via the dimensions of the resonator, provided the mode is well identified. In the classic experiment of Moldover and colleagues [1] that paved the way for the more recent campaign of measurements, gravimetric weighing was used to determine the resonator's volume and thereby the effective radius. A more modern method, which allows real-time monitoring of the dimensions, is microwave resonance. Since it is impossible to make a perfectly spherically shaped resonator, a quasi-spherical shape, specifically, the tri-axial ellipsoid, is used instead. The lengths of the semi-major axes are made slightly different (by a few tenths of a millimeter) such that the three microwave resonances corresponding to the lowest-order orthogonal modes can be resolved. An effective radius $a = (a_x a_y a_z)^{1/3}$ is then used to calculate acoustic velocity. In reality, the non-spherical shape leads to correction terms and it is only thanks to their analytical calculation by Mehl [28] that the accuracy of modern determinations of k has been made possible.

To excite and detect the microwave modes, one has the choice of straight (or pin) or loop antennae. The latter were found to be preferable since, in addition to providing a greater signal amplitude, they allow one to excite both TE and TM modes. The comparison of the linewidth of these modes provides information on surface effects and skin depth.

The main correction for acoustic thermometry using a spherical resonator is the boundary layer correction in the acoustic frequency resonance, around 100 ppm (i.e. about 100 times the target uncertainty for k). This effect is due to the difference of four orders of magnitude in heat capacity between the shell and the gas. Thermal oscillations in the acoustic wave are produced as it meets the resonator wall that cannot change its temperature due to its larger heat capacity. The effect, called the boundary layer effect, depends only on the thermal conductivity of the gas, its density and its heat capacity. These quantities are given by *ab initio* calculations. Such calculations have provided more independence of results with respect to a specific experiment, made measurements more widely accepted, and allowed one to imagine future measurements over a wider range of temperature than that explored heretofore.

The second largest correction is related to shell vibration, which results from the mechanical interaction of the oscillation of the acoustic wave with the internal mode of the structure of the shell. Shell resonances depend on the size and thickness of the resonator. Their frequencies can be estimated analytically [29] if one supposes the shell to be made in one piece and not from two hemispheres, or by finite element modeling, which is used in the design of resonators. For the stainless-steel resonator used in Moldover's measurement, the agreement is better than 1% [1]. However, for copper, the metal used in most modern experiments, the agreement is no better than 5% [30]. In acoustic thermometry, several acoustic resonances are usually studied. In some cases, however, the proximity of an acoustic mode to a shell resonance perturbs the data for that mode to an unacceptably large extent. Note that this effect vanishes as the pressure is decreased. It is mainly due to this last point that the measurement of the speed of sound is extrapolated to zero pressure. The *ab initio* calculation of the gas polarizability offers the possibility to check in real time if the radius measurement made by microwave resonance is correct.

In the most accurate determinations of k , the main components in the uncertainty were comprised of five, almost equal elements [10,7]. This confirms that AGT has reached a limit not likely to be surpassed for many years. (To reduce

the uncertainty, one needs to work in parallel to reduce all contributions by the same amount, which is very hard.) We emphasize that the largest of these is the realization of the definition of the temperature unit, i.e. the triple point of water.

While we have focused on quasi-spherical resonators, we note that another geometry, cylindrical, was used by the group at NIM to provide a value of k that contributed to the CODATA adjustment [9]. Here the longitudinal modes of the cylindrical resonators are the ones used to measure the speed of sound. The length of the resonator was measured by optical interferometry in the earlier experiments, then by microwave resonance. To eliminate effects due to deviations from perfect geometry, the group used two cylinders of different lengths with the same endcaps. Due to unexpectedly high instrumental noise, the group was unable to achieve the required sub-3-ppm accuracy from its most advanced measurement. However, a global average of several results, with allowance for correlations between experiments, yielded the value used by CODATA. The same approach was used in dielectric constant gas thermometry (DCGT), the technique that provided the next most accurate measurements of the Boltzmann constant after AGT.

3.2. Dielectric constant gas thermometry

In dielectric constant gas thermometry [25], the relative electric permittivity or dielectric constant of a gas $\varepsilon_r(p)$ is measured as a function of pressure to determine the temperature. The technique is related to refractive index gas thermometry (RIGT) where the speed of electromagnetic waves in a gas and *in vacuo* are compared. To determine Boltzmann's constant, measurements are performed at a known temperature (T_{TPW}), and the value of k extracted from the Clausius–Mossotti relation, modified by the appropriate virial terms [23]. The principle is straightforward enough: measure the capacitance $C(p)$ of a capacitor in a gas and its value under vacuum $C(0)$ and take the ratio to extract the value of ε_r . Then deduce a value of k from ε_r using the known molar polarizability A_ε and density and dielectric virial coefficients. The technique lies in a sense mid-way between AGT and JNT in that it uses a well-characterized noble gas and pressure measurements at the frontier of accuracy, as well as primary level electrical metrology to measure minute changes in already tiny capacitances (≈ 10 pF).

The quantity measured in the experiment is

$$\gamma = \frac{C(p) - C(0)}{C(0)} = \varepsilon_r - 1 + \varepsilon_r k_{\text{eff}} p \quad (2)$$

where k_{eff} is the effective compressibility of the capacitor assembly. Defining the dimensionless parameter $\mu = \gamma/(\gamma + 3)$, one can write the virial expansion for the pressure p as

$$p = A_1(\mu + A_2\mu^2 + A_3\mu^3 + \dots) \quad (3)$$

where

$$A_1 = \left(\frac{A_\varepsilon}{RT} + \frac{k_{\text{eff}}}{3} \right)^{-1} \quad (4)$$

and

$$A_\varepsilon = \frac{N_A \alpha_0}{3\varepsilon_0} \quad (5)$$

The coefficients A_2 and A_3 are related to the second and third density and dielectric virial coefficients describing two- and three-body interactions. A fit of the expansion (3) to an isotherm measured at a temperature T gives the ratio A_ε/R . The Boltzmann constant k is then obtained via

$$k = \frac{\alpha_0}{\varepsilon_0} / \frac{A_\varepsilon}{R} \quad (6)$$

The electric dipole polarizability has been calculated for the ground state 1S_0 of helium-4 with a relative uncertainty of less than 0.1 ppm [31].

In this technique, as in RIGT, the difficulty is to allow correctly for the compression of the capacitor as the pressure is changed. To minimize the effect, in the most accurate determination of k by DCGT [8], the cylindrical measuring capacitor was made from tungsten carbide, the isothermal compressibility of which is roughly half that of stainless steel, the material used in earlier measurements.

In DCGT, the choice of gases is slightly broader than for acoustic thermometry, since isotopic abundance is not a critical parameter. Whereas molecular mass has a direct impact on acoustic velocity, its influence on dielectric properties, via isotopic shifts of energy levels, is far smaller. In the DCGT experiments used for the final determinations of k only helium was employed since its polarizability is known the most accurately. The polarizability is so small, however, that its determination by experiment lies at the limits of the possibilities of primary electrical metrology. (The relative capacity change must be measured with an uncertainty of a few parts in 10^9 .) For the heavier, more polarizable noble gases, the experimental determination gets easier, but the *ab initio* calculation becomes more difficult due to the more complex electronic structure. It is expected that, ultimately, theory will overtake experiment for the polarizabilities of all the noble gases.

Note that although isotopic abundance is not a critical parameter in DCGT, gas purity is. For this reason, gas samples were analyzed by mass spectrometry after each measurement campaign.

The *ab initio* calculation of the polarizability and its virial density expansion of helium [31] allowed the PTB experiment [8] to be competitive for the determination of k . The properties of helium were also used in the hydrostatic correction between the pressure sensor and the capacitance used to estimate the dielectric constant of helium.

One of the toughest tasks in the experiment was the accurate measurement of absolute pressure (uncertainty equal to 1 ppm [32], which is two to three times better than the best uncertainty obtained by the NIST group [33]). The ultimate challenge, however, was the determination of the compressibility of the capacitor as a function of the applied pressure. This effect was the one of the two main components in the uncertainty budget along with the dispersion of the results i.e. the type-A uncertainty. The final results submitted to CODATA by the PTB group [8] were the weighted averages of the last three measurements, with careful allowance for correlation.

Although two different methods to determine k to 3 ppm or better would have sufficed to satisfy the CCT requirement, it is comforting that a third, gas-free technique, Johnson Noise Thermometry (JNT), was also able to provide input data for CODATA adjustment.

3.3. Johnson noise thermometry

In Johnson noise thermometry, the gas is one made of molecules in a vessel but rather of electrons in a resistance R_{JNT} . The unilateral voltage power spectrum $\overline{U^2}$ measured in a bandwidth $d\nu$ for a resistance R_{JNT} maintained at a temperature T is given by

$$\overline{U^2} = 4h\nu R_{\text{JNT}} d\nu / (e^{h\nu/kT} - 1) \quad (7)$$

At ambient temperature and for frequencies up to 100 MHz, the denominator is equivalent to $h\nu/kT$ to better than 10^{-9} , so the equation simplifies to the well-known Johnson–Nyquist formula [34,35] given by equipartition:

$$\overline{U^2} = 4kT R_{\text{JNT}} d\nu \quad (8)$$

Johnson noise is often a limiting factor in many experiments that can be reduced either by narrowing the measurement bandwidth $d\nu$ or lowering the temperature T or both. In experiments to measure k using Johnson noise, the aim is to maximize it! Since the temperature T is fixed at T_{TPW} , the remaining variables are the value of the resistance R_{JNT} and the bandwidth $d\nu$. In the most accurate work, the noise from the source resistance is compared with that of a calibrated source based on a Josephson junction array. A critical aspect of the measurements is to match the impedance of the resistance with that of the array. In the NIM–NIST experiment, the self-calibrating noise source fabricated by NIST has an impedance of 100 Ω , so a source resistance of identical value was used. The aim is to make the noise source correspond as ideally as possible to a pure resistance, such that the noise spectrum is flat. In practice this is impossible, which limits the bandwidth to far less than the 100 MHz seemingly allowed by the ratio $h\nu/kT$. The experiment measures the ratio of the noise power from the sensing resistance to that of the calibrated noise source. This ratio falls with increasing bandwidth. Fits of the noise power ratio as a function of frequency agreed to within $\pm 1\sigma$ (standard deviation) for different bandwidths of up to several hundred kilohertz. In the most accurate determination of k by JNT [11], the ambiguity in results obtained for different bandwidths was the largest cause of non-statistical uncertainty (1.0×10^{-6}).

While the name of the game might be to maximize Johnson noise, it goes without saying that all other sources of electrical noise must be reduced to a negligible level. To do this, many of the techniques developed for state-of-the-art electrical metrology are used [36]. All instruments are powered by batteries that have often to be replaced. Circuits are housed in aluminum boxes with high-permeability nickel alloy shields. Signals are transmitted via optical fibers to avoid ground loops. In the experiment that provided the most accurate data [11], the apparatus was housed in an underground screened room on a remote campus, far from the center of Beijing. Measurements were performed with the lights turned off and the door locked. On the other hand, with only a small resistance on a circuit board as the element to be thermalized, the thermometry was far simpler than in other determinations of k , employing a standard triple-point water cell whose ice–water mixture was changed daily. Even with optimal signal-to-noise ratio, measurement times were very long – 100 days of useful data acquired over a 120-day period [11]. The relative experimental uncertainty, 2.7×10^{-6} , was essentially limited by statistics (2.37×10^{-6}), so to gain a further factor of two in accuracy would have required over a year of data acquisition. To improve the apparatus in view of thermometry at T_{TPW} and above, the most obvious step would be to increase the size of the source resistance by developing a Josephson junction noise voltage standard of higher impedance. In addition, while the source resistance obviously should not be cooled, noise in the amplifier linked to it (1 nV/Hz^{1/2}) could, in principle, be reduced twofold by operating it at liquid nitrogen temperature (77 K) [37].

Although ultimately unable to provide a measurement of k at the required 3 ppm level of accuracy before the CCT deadline, a fourth method, Doppler-broadened molecular spectroscopy, might one day approach such a limit in terms of thermometry.

3.4. Doppler-broadened molecular spectroscopy

Pioneered by C. J. Bordé and colleagues at the ‘Université Paris-Nord’ [38], the method uses the measurement of the Doppler width of a spectral line in a gas at a known temperature to determine a value for the Boltzmann constant.

In the absence of homogeneous broadening, the full-width at half-maximum $\Delta\nu$ of a spectral absorption line of frequency ν_0 is given by

$$\Delta\nu = 2\nu_0(2 \ln 2 kT/mc^2)^{1/2} \quad (9)$$

where m is the molecular mass. Molecular masses are known to around 10^{-8} in relative value thanks to measurements of the ratio h/m_{CS} [39] and h/m_{Rb} [40] by atom interferometry, and ratios of atomic and molecular masses [41].

In its simplest form, the lineshape of an absorption resonance in an atom or molecule, for a unidirectional laser beam, is a Voigt profile, the convolution of a Gaussian profile resulting from Doppler broadening with a Lorentzian component related to spontaneous emission and especially collisional broadening. At low pressures, the so-called impact regime prevails, whereby the duration of a collision is much shorter than the time between collisions, itself far less than the spontaneous emission lifetime. The result of a collision is to de-phase the radiating molecular dipole. For a given velocity class, the Fourier transform of the electric field gives rise to a broadened Lorentzian lineshape. In the case of the molecules studied to determine the Boltzmann constant, the natural linewidth is negligible, but collisional broadening cannot be ignored. To a first approximation, the collisional width is proportional to the gas pressure. Thus, by making measurements at different pressures and extrapolating to zero pressure, one could remove it.

The real situation is of course more complicated. First, obviously, the lower the pressure, the smaller the absorption signal, so, as in AGT, measurements at lower pressures are the least accurate. Moreover, the absorption profile is modified by velocity-changing collisions. Dicke narrowing [42] leads to a decrease in linewidth with pressure. As the pressure is increased, the Voigt profile no longer provides an adequate description, so more sophisticated models with extra parameters must be used. The ‘Paris-Nord’ group used the Galatry or soft-collision model. In relation to this work, an interesting, by no means obvious feature of absorption spectroscopy, was discovered by Bordé [43]. This is, for an isotropic distribution of molecular velocities, the lineshape is independent of laser beam geometry, i.e. transit-time effects are already included in the Doppler width. Another aspect concerns the measurement of the absorption linewidth, even before analysis. In most spectroscopic experiments, one measures the central frequency of an absorption profile. In this case, a flat background has no effect on the result, while a linearly sloping one can be removed using third-harmonic phase-sensitive detection. With a linewidth measurement, any background is a source of systematic uncertainty. For this reason, it is important to use as isolated a resonance as possible because the wings of neighboring components, even weak ones, affect the measured linewidth. For the same reason, scans over the resonance should cover many linewidths to establish the baseline. A further subtle effect was shown to be increased linewidth caused by the finite bandwidth of the detector in the case of a first-order filter [44].

Below we consider the experiments in turn. All of them consist in the measurement of a Doppler width for a sample maintained at a temperature very close to T_{TPW} . As for the measurement of k by other methods, thermometry would limit the uncertainty to around 0.3 ppm. Unlike the case of acoustic gas thermometry and dielectric constant gas thermometry, where the choice of gas species is very limited, in principle, very many different atoms or molecules could be used for Doppler broadening thermometry. Small, simple, non-polar ones would appear to be the best choice: the lighter the species, the greater the Doppler width at a given temperature; moreover, the lighter molecules have more widely separated rovibrational transitions than do heavy molecules. Non-polar molecules (O_2 , CO_2 , C_2H_2) have lower collisional self-broadening than polar ones. In the case of CO_2 , low transition strengths at accessible wavelengths were a handicap [45]. Ultimately, the choice made by the groups measuring the Boltzmann constant was often guided by history, previous knowledge of molecular structure and the equipment developed at the wavelength concerned. The results are listed in Table 1.

The first reported measurement of the Boltzmann constant by laser spectroscopy was by Daussy et al. [38], who obtained a value in accordance with the CODATA value of the time. The uncertainty was 200 ppm. They measured the Doppler width of the ν_2 saQ(6, 3) rovibrational line of the ammonia molecule $^{14}\text{NH}_3$ at a frequency near 29 THz. The transition was chosen not only because it was isolated, but also because the frequency was accessible to the ultra-stable CO_2 lasers developed by the group over the preceding decades. (A group starting out to measure k would probably not otherwise choose to use carbon dioxide lasers in the mid-infrared.) It was announced that improved measurements would later contribute to the new definition of the kelvin. Indeed, the experimental accuracy did improve, but not as quickly as predicted. The 38-ppm uncertainty of Djerroud et al. [46] was later realized to be an underestimate owing to lineshape effects. Cygan et al. [47] pointed this out in a theoretical study of dioxygen. A new measurement on ammonia with a total uncertainty of 144 ppm was later published by the ‘Paris-Nord’ group, though type-A uncertainty was an encouraging 6.4 ppm [48]. The lesson learnt from these measurements was that to avoid pressure-related systematic effects, the ammonia gas pressure should not exceed 0.5 Pa. For pressures lower than this, the lineshape was considered to be sufficiently well understood. Indeed, in subsequent articles by the same group [49,50], a relative achievable type-B uncertainty of 2.3 ppm was reported. However, no experimental value for k was forthcoming before 31 July 2017, the deadline for inclusion in the final CODATA adjustment.

Following an earlier, proof-of-principle measurement using carbon dioxide [45], the Second University of Naples group [51] switched to water, in particular, to a line near 1.4 μm in the vibration rotation spectrum of the molecule H_2^{18}O . This

Table 1
Determinations of k by Doppler broadening thermometry.

Reference	Species	k (10^{-23} J·K ⁻¹)	u_k/k (ppm)
[38]	¹⁴ NH ₃	1.38 65(26)	190
[46]		1.380 669(52)	38
[48]		1.38 080(20)	144 of which 6.4 (type A)
[50]		–	2.3 (type B est.)
[45]	¹² CO ₂	1.380 58(13)	160
[51]	H ₂ ¹⁸ O	1.380 631(33)	24
[54]	¹³ C ₂ H ₂	1.394 0(17)	1200
[55]	¹² C ₂ H ₂	1.380 66(12)	87
[60]	⁸⁵ Rb	1.381 04(59)	430

heavier isotopologue (natural abundance 0.205%) was chosen to avoid absorption of the laser beam by atmospheric water vapor (99.757% H₂¹⁶O). One might suppose the even rarer isotopologue H₂¹⁷O (abundance 0.038%) was avoided because of hyperfine structure arising from the non-zero spin ($I = 5/2$) of the ¹⁷O nucleus. The choice of a line near 1.4 μm has some advantages compared with the mid-infrared range as regards less expensive, more convenient light sources, optics, and detectors. Moreover, due its environmental importance, the water molecule has been studied intensively for decades. Making measurements in a cell at a temperature 5 mK below T_{TPW} , the group determined a value of k with an overall uncertainty of 24 ppm, the best to date for optical measurements of the constant. Aside from temperature control and measurement, another key element in the success of the experiment was laser intensity stability ($<10^{-4}$) over the scanning range of 3.1 GHz used to acquire profiles. The dominant source of uncertainty in the experiment was due to the lineshape for which even a speed-dependent Voigt profile was shown to be inadequate. Values of k obtained with this and the more complete partially-correlated, speed-dependent hard collision (pcSDHC) model differed by 700 ppm. As with the work on ammonia, the key to improved accuracy was believed to be measurements at lower pressures, with a longer path length to compensate for the reduced linear absorption coefficient.

Following the end of the experimental campaign, further theoretical studies were performed by the same group, notably concerning the importance of hyperfine structure [52]. These showed that neglecting hyperfine structure would modify the value of the Boltzmann constant by 4×10^{-8} , roughly two orders of magnitude smaller than the lowest experimental uncertainty. For a molecular velocity $v \approx 500$ m·s⁻¹, roughly 1.6×10^{-6} times the velocity of light c_0 , relativistic effects were stated to be negligible based on a study of a relativistic Voigt profile [53]. Naively, given that for a transition frequency ν_0 , the relativistic Doppler shift $(-v^2/2c_0^2)\nu_0$ of a molecule of speed v is smaller than the first-order shift by a factor $v/2c_0 = 0.8 \times 10^{-6}$, one might expect it necessary to take it into account for a measurement at the 1 ppm level of accuracy.

Acetylene, another simple molecule accessible with laser diode sources, was investigated both in absorption spectroscopy [54,55] and cavity ring-down spectroscopy [56]. The latter technique is known for its high sensitivity though, as with all other optical determinations of k , the main difficulty is not the signal-to-noise ratio, but rather the detailed understanding of the composite lineshape. An advantage of acetylene over ammonia and water is that it is non-polar. Yamada and colleagues [54] studied the P(16) transition in the $\nu_1 + \nu_3$ band near 1.56 μm . The isotope-substituted ¹³C₂H₂ was chosen because the frequency of the line in question had previously been determined with great accuracy [57]; it lies close to half the frequency of the two-photon transition near 778 nm in Rb [58] used for some determinations of the Rydberg constant [59]. The uncertainty in the value of the Boltzmann constant, some 1200 ppm, was due mainly to the temperature measurement ($T = 295.65(30)$ K). Later, Hashemi and colleagues studied the P(25) line in the same band ($\lambda = 1.54$ μm), but with the common isotopologue ¹²C₂H₂. Spectra recorded for an average cell temperature of 295.78 K and for pressures from 33 Pa to 670 Pa were fitted to a speed-dependent Voigt profile. Values of the Doppler width were found to be independent of pressure over the range explored. The overall measurement uncertainty in k , 87 ppm was dominated by the temperature measurement. In the single-pass, 1.54-m-long absorption cell, obtaining a uniform temperature was a major challenge. The relative systematic error for k was only 19 ppm.

While alkali atoms such as caesium and rubidium might be an attractive option for Doppler thermometry, their very low vapor pressure at T_{TPW} was a drawback for a determination of the Boltzmann constant [60]. They also display a higher sensitivity to magnetic fields than do molecules, and one must allow too for optical pumping between hyperfine levels of the ground state. Alkali atom Doppler thermometers are emerging rather as convenient, less accurate devices for measurements at room temperature and above, e.g., in atom chip devices [37].

As with the other techniques used to measure the value of k , the story will not end with the new definition of the kelvin. The experiments become thermometers in which the Doppler width yields the temperature. To perform absolute Doppler broadening thermometry with an accuracy of 1 ppm would however be an exceedingly tall order. To put this into perspective, we shall draw a parallel with state-of-the art time and frequency metrology. It is more difficult to measure a linewidth than to find the center of a line, the latter being affected by asymmetry, but not by the overall shape. The best studied of all atomic or molecular transitions is the $F = 3$ to $F = 4$ hyperfine transition in Cs at 9.2 GHz used to define the SI second since 1967. It is measured with a relative frequency uncertainty in the low 10^{-16} s. This represents a few ppm of the 1 Hz linewidth observed in most primary Cs fountain clocks. Such an uncertainty, for a well-characterized atom studied in very clean conditions, is the fruit of decades of effort by several leading primary laboratories. For a handful of groups

studying different molecular transitions, to have reached an uncertainty in Doppler thermometry of tens of parts per million after only ten years or less is already a considerable achievement.

4. Perspectives: more accurate thermometry over a wider, more continuous range

Since 1650 and the work of Ferdinando II de' Medici [61], a phase transition of water (freezing point or triple point) has formed the basis of thermometry. For the past century or more, the standard in thermometry has been based for the most part on the use of resistance thermometers, especially the platinum resistance thermometer [62]. These standard thermometers have proved to be extremely stable over time and over the temperature cycle when their resistance is re-measured at the triple point of water. One should note, however, that in recent years the quality of these thermometers has fallen as is evident in the last two key comparisons in thermometry, CCT-K3 [63] and CCT-K9 [64]. The need for a new standard is ever more pressing.

Standard platinum resistance thermometers are used to perform thermometry in a more repeatable, easy-to-install way than first-principles thermometers yielding thermodynamic temperature. Indeed, instead of requiring days of averaging and the analysis of complex data, a simple measurement of resistance can be used. However, such resistances need to be calibrated because for the moment there is no first principles relation between the electrical resistance and the thermodynamic temperature of platinum [65]. The standard platinum resistance thermometer is used to maintain practical temperature scales in the range from 13.81 K (the triple point of di-hydrogen) to 961.78 °C (the freezing point of silver). These devices are calibrated using artefacts, fixed-point cells containing pure substances (pure elements or water) whose phase transitions (melting, freezing or triple points) have been ascribed exact temperatures. An international practical temperature scale (ITS), revised from time to time [62], specifies continuity between fixed points via the use of a polynomial, the degree of which depends on the temperature region in question. While thermometry at the 0.1-mK level is possible at or within a few degrees Celsius of fixed points, uncertainty levels rise in between them due to the non-uniqueness of the polynomials and the propagation of fixed-point uncertainties [66]. Moreover, the ITS has no fundamental physical basis. With the new definition of the kelvin, even though T_{TPW} will be ascribed an uncertainty of 0.1 mK (as opposed to none before the redefinition), it will be possible to measure thermodynamic temperature at the sub-millikelvin level of accuracy over a continuous temperature range of several hundred kelvin. Acoustic thermometry can be used from a few kelvins up to 500 K, the current upper limit on temperature being the availability and performance of high-temperature transducers. Constant-pressure refractive index gas thermometry of helium will provide increasingly more accurate measurements at low temperatures (with the improvement of *ab initio* calculations) [67]. At high temperatures (≥ 1000 K) Johnson noise thermometry should prove a valuable complement to optical pyrometry. For practical reasons, it is likely that an ITS based on current fixed points (some with adjusted values) or some new ones will exist for some time. Indeed, an important spin-off of work on the Boltzmann constant has already been the (re-) determination of the thermodynamic temperatures of several fixed points, which will lead to a more coherent version of the scale.

Acknowledgements

The authors acknowledge helpful discussions with Jifeng Qu, Jintao Zhang, and Stéphan Briaudeau. LP and MP are grateful to Bo Gao of the Technical Institute of Physics and Chemistry of the Chinese Academy of Sciences, and Jintao Zhang of NIM, China in whose laboratories much of this article was written. The French AGT work described was partly funded by the European Metrology Research Program (EMRP) project InK2 (No. 15SIB02). The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

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