

Workshop on Methods for New Determinations of the Boltzmann Constant

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Introduction

On January 21, 2005, a workshop on methods for new determinations of the Boltzmann constant k was held at PTB. It gave an overview of the state-of-the-art of thermodynamic temperature measurements at temperatures near the triple point of water T_{TPW} . In this document, primarily the progress compared to the status described in [1] and some other new developments are discussed. The currently available CODATA recommendation of the value $k = 1.3806503(24) \times 10^{-23}$ J/K based on acoustic gas thermometry at NIST, is already documented in [2] and is, therefore, not repeated here.

The methods for determining the Boltzmann constant are discussed in this document applying the following classification:

- Acoustic gas thermometry (AGT),
- Thermal-equation-of-state methods,
- Radiation thermometry,
- Methods based directly on statistics and quantisation.

Acoustic gas thermometry (AGT)

The determination of the Boltzmann constant applying AGT is based on the relation

$$k = \frac{Mu_0^2}{N_A \gamma_0 T_{\text{TPW}}}$$

valid for an ideal gas, where M is the molar mass of the gas used; u_0 is the zero-frequency, zero-pressure limit of the speed of sound; N_A is the Avogadro constant; and γ_0 is the zero-pressure limit of the heat-capacity ratio c_p/c_V . Advantages of AGT are the second-order influence of pressure measurement and the low influence of the deformation of the apparatus under pressure. Mike Moldover, NIST, analysed at the workshop the state-of-the-art measurement techniques and claimed that a relative uncertainty of k of one part in 10^6 (1 ppm) could be obtained if they would be used to repeat the experiments at NIST described in [3, 4]. The main uncertainty components with the estimated limits of the standard uncertainty in parenthesis are: determination of the dimensions of the spherical resonator (0.39 ppm), traceability to the TPW (0.36 ppm), molecular weight of the measuring gas argon (0.42 ppm), and zero-pressure limit of and corrections to frequency (0.69 ppm). For the first component it might be problematic that all determinations of the density of mercury used for measuring the volume of the resonator are many years old and a new determination with the necessary accuracy is currently world-wide not possible. The use of helium as alternative measuring gas was proposed because the number of necessary parameters in the virial expansion is smaller and because the uncertainty of the molecular weight is negligible.

In their talks Piero Marcarino and Roberto Gavioso described that new AGT measurements will be performed in a collaboration of IMGC and IEN to determine the Boltzmann constant. It is intended to derive the dimensions of the spherical resonator from the resonance frequencies of microwave modes in the resonator. Several microwave modes will be used to evaluate the perturbations of the microwave modes due to different effects. The uncertainty of the final result is not known at

present. In [5], even the mode-dependent deviations of the calculated radius values were of order 10 ppm.

Thermal-equation-of-state methods

Methods for determining the Boltzmann constant based on the thermal equation of state of ideal gases are for instance:

- Constant volume gas thermometry (CVGT),
- In-situ measurement of the gas density via the dielectric constant ε or the refractive index n (combination of the thermal equation of state with the Clausius-Mossotti equation): dielectric-constant gas thermometry using audio-frequency capacitance bridges (DCGT), measurement of ε with microwave quasi-spherical cavity resonators (QSCR) operating at gigahertz frequencies, and refractive index gas thermometry (RIGT) applying optical resonators,
- Density measurement.

The application of CVGT was not discussed during the workshop. In view of the information available in literature it seems at present not possible to reach an uncertainty level essentially smaller than 10 ppm [1].

On the contrary, DCGT has the potential to reach a level of order 1 ppm comparable with that of AGT. It is based on the relation

$$k = \frac{\alpha_0}{\varepsilon - \varepsilon_0} \frac{p}{T_{\text{TPW}}} = \frac{R}{A_\varepsilon} \frac{\alpha_0}{3\varepsilon_0}$$

with the molar gas constant R , the molar polarizability A_ε , the static electric dipole polarizability of the gas particles α_0 , and the exactly known electric constant ε_0 . For the measuring gas helium, the ab initio calculations of α_0 have nowadays an uncertainty well below 1 ppm as explained by Krzysztof Szalewicz, University of Delaware, in his talk (cf. [6]). Bernd Fellmuth, PTB explained that the ratio R/A_ε can be determined by extrapolating isotherms measured at the TPW to zero pressure [7]. Since the dielectric susceptibility $\chi = \varepsilon/\varepsilon_0 - 1$ of helium is very small ($7 \cdot 10^{-5}$ at 0.1 MPa and at the TPW), it is not possible to measure ε absolutely, rather the relative change $(C(p) - C(0))/C(0)$ of the capacitance C of a capacitor due to the measuring gas with pressure p is determined. The discussion confirmed that main uncertainty components result from the measurement of relative capacitance changes and pressure as well as from the deformation of the capacitor under pressure. Relative standard estimates of these three components for the state-of-the-art equipment at PTB are 3 ppm, 5 ppm, and 13 ppm, respectively.

For achieving an uncertainty of the determination of k of order 1 ppm, the influence of the uncertainty on the measurement of capacitance changes can be decreased by improving the parameters of the audio-frequency capacitance bridge and by working with higher pressures up to about 7 MPa. This requires improving pressure balances, the effective area of which is calculated from dimensional measurements and from considering the distortion under pressure. For pressure balances with an effective area of 5 cm² an uncertainty level of 5 ppm has been achieved [8]. Though up to now international intercomparisons could not verify this level, it is well supported up to 2 MPa by a comparison with a high-pressure mercury manometer and comparisons of quite different pressure balances. The compared pressure balances made by different manufactures had different designs and widths of the gap between piston and cylinder, different sources of the piston-cylinder materials (tungsten-carbide), and were operated with gas and oil, respectively [9]. Further progress is expected applying pressure balances with larger effective areas and new length-measurement techniques.

Due to the deformation of the capacitor under pressure, the relative change of the capacitance is given by $(C(p)-C(0))/C(0) = \chi + (\mathcal{E}/\epsilon_0) \kappa_{\text{eff}} p$. The effective compressibility κ_{eff} considers that the capacitor must be built using different materials and has an order of magnitude of a few $10^{-12}/\text{Pa}$. Today, the compressibility of hard solids (e.g. tungsten carbide) can be determined with a relative uncertainty of approximately 0.1%, which corresponds to an uncertainty of χ of order 10 ppm. Thus, sophisticated methods must be applied for decreasing the influence of the deformation under pressure. The construction materials have to be optimised and the deformation measured in-situ, e.g. using specially designed cylindrical capacitors and interferometric measurements or spherical capacitors. Furthermore, it is helpful to have the same pressure in the surroundings as in the capacitor.

The application of QSCRs for measuring the dielectric constant was briefly discussed during the workshop, but feasibility tests are presented in [10]. Measurements with helium at 289 K and at pressures up to 7 MPa yielded ϵ values that coincide within about 0.2 ppm with the calculated ab-initio ones, corresponding to an uncertainty of k of about 40 ppm at the highest pressure. The results of dimensional measurements differed from those of microwave measurements by the same order of magnitude. A proof-of-principle for RIGT is described in [11]. Using helium to correct for pressure-induced distortions of two refractometers, the results obtained with the two systems for the refractive index of nitrogen agree with each other within a few parts in 10^9 (ppb). It is hoped that with more substantial and additional effort a level of order 0.1 ppb can be achieved. This would correspond to 1 ppb for helium at room temperature and 0.1 MPa, i.e. 30 ppm for k . But for the determination of the Boltzmann constant, helium must be used as the measuring gas and can, therefore, not be used to correct for the pressure-induced distortions.

Another thermal-equation-of-state method could be to measure the high-pressure density of a gas using densimeters with silicon sinkers [12], but at present it is not known whether an uncertainty of order 10 ppm or lower can be achieved.

Radiation thermometry

A primary thermometer applicable also for determining k is based on the Stefan-Boltzmann law and measures the total radiation without spectral selection using a cryogenic radiometer. This method has been developed at NPL, UK. Quinn and Martin [13] have obtained results between -130 °C and 100 °C and gave a relative standard uncertainty estimate for k measured at the TPW of 32 ppm. The main contributions to this uncertainty were from the thermal radiation transfer function (25 ppm), diffraction (18 ppm), absorption of the aperture land (5 ppm), and scatter (5 ppm).

Recently NPL has built a new version of a total radiation thermometer (TRT), which is expected to measure the Stefan-Boltzmann constant with an uncertainty of 20 ppm and, with reference to the TPW, thermodynamic temperatures between the mercury (234 K) and tin (505 K) fixed points [14] with uncertainties of around 0.5 mK. A determination of the Stefan-Boltzmann constant with a relative uncertainty of 20 ppm corresponds to a determination of the Boltzmann constant k with an uncertainty of 5 ppm. In his talk Nigel Fox, NPL, analysed the potential to reach the envisaged uncertainties and reported especially how to solve the difficulties with the radiation trap connecting the blackbody and the detector. Taking into account the main uncertainties sketched above, a determination of the Boltzmann constant with a reliable relative uncertainty of 5 ppm would certainly have to be considered a major advance of absolute radiation thermometry.

Spectral radiation thermometry (SRT) on the basis of Planck's radiation law needs cryogenic radiometers to establish scales of spectral responsivity. The additional uncertainty of the calibration of the spectral responsivity of the transfer filter radiometer has to be taken into account, which cannot be lower than the uncertainty of the cryogenic radiometer used for calibration. Altogether,

this results in best relative uncertainties at the level of 100 ppm at temperatures of about 500 °C and above and wavelengths between 650 nm and 1000 nm [15-17]. Since the uncertainty will not diminish with decreasing temperature, 50 ppm is presently considered a realistic estimate for the relative uncertainty of k that can be reached by measurements at the TPW.

Spectral radiation measurements, even if they are not expected to reach comparably small uncertainties, will support the redefinition of the kelvin. In addition, spectral radiation measurements are considered to be the only method which is capable of disseminating the temperature scale based on the new definition directly to the users, especially at high temperatures. This would avoid the troublesome error propagation of the current definition.

Methods based directly on statistics and quantisation

Applying the Nyquist formula, Johnson noise thermometry (JNT) at the TPW can be used for determining the Boltzmann constant, but an uncertainty level of 10 ppm seems to be a true challenge [18,1].

Stéphan Briau and Christian Chardonnet presented the idea of the determination of k by measurements of the Doppler broadening of laser absorption in an equilibrium gas cell within a collaboration of BNM-INM/CNAM and the University of Paris North, France. Doppler broadening measurements are a standard means of diagnostics for high-temperature plasmas. In this field of application, uncertainties are at the percent level or even higher [1]. The feasibility of the determination of k was discussed, and in the meantime first Doppler profiles were recorded. Essential uncertainty components result from temperature control and measurement, absorption of laser power and external heating, influence of the interaction of the gas particles and the finite mean free path, and non-linearity of the effect but to estimate the potential of the method reliably more experimental work is required.

New routes towards determinations of the Boltzmann constant are discussed in the Quantum Metrology Programme of the NPL, UK [19], including novel methods based on single electron tunnelling and phonon spectroscopy in the quantum limit. At present, the feasibility of these routes is not known.

Summary

Though the uncertainty estimates given above are not in all cases based on complete budgets, the following table gives a summary overview of the potentials of the available primary thermometers for determining the Boltzmann constant k , as deduced from the workshop and recent information on new developments. The table illustrates that the mid-term possibility within the next five years is to achieve a reliable uncertainty of the k value of order 1 ppm based on measurements applying different methods of primary thermometry.

Summary table: Uncertainty of determining the Boltzmann constant applying different methods of primary thermometry, see the text for the meaning of the estimates.

Method	Present state	Mid-term possibility
AGT	2 ppm	1 ppm
DCGT	15 ppm	2 ppm
TRT	32 ppm	5 ppm
SRT		50 ppm
JNT		10 ppm
QSCR	40 ppm	10 ppm
RIGT	300 ppm	30 ppm

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