

## Research



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# Progress towards the determination of thermodynamic temperature with ultra-low uncertainty

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Previous research effort towards the determination of the Boltzmann constant has significantly improved the supporting theory and the experimental practice of several primary thermometry methods based on the measurement of a thermodynamic property of a macroscopic system at the temperature of the triple point of water. Presently, experiments are under way to demonstrate their accuracy in the determination of the thermodynamic temperature  $T$  over an extended range spanning the interval between a few kelvin and the copper freezing point (1358 K). We discuss how these activities will improve the link between thermodynamic temperature and the temperature as measured using

the International Temperature Scale of 1990 (ITS-90) and report some preliminary results obtained by dielectric constant gas thermometry and acoustic gas thermometry. We also provide information on the status of other primary methods, such as Doppler broadening thermometry, Johnson noise thermometry and refractive index gas thermometry. Finally, we briefly consider the implications of these advancements for the dissemination of calibrated temperature standards.

## 1. Introduction

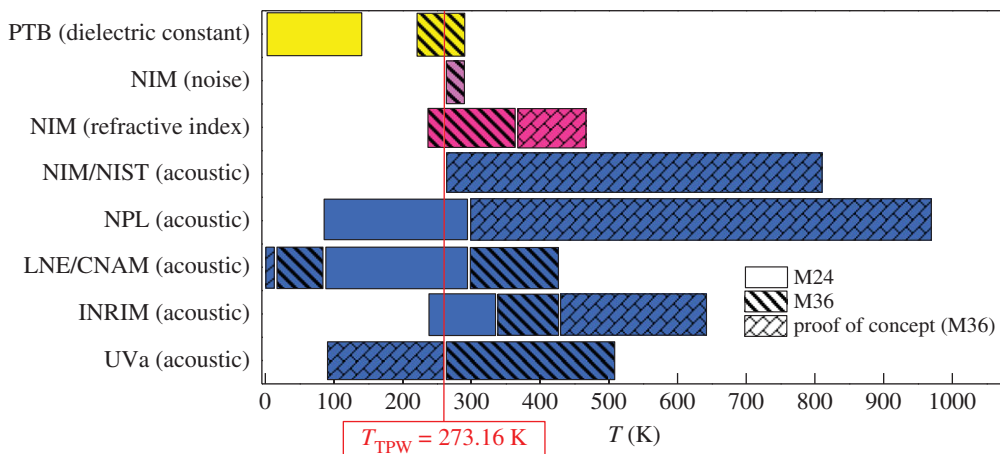
The quest for achieving ever more accurate determinations of the Boltzmann constant  $k$ , to support a new definition of the kelvin, has proved an efficient driver towards the improvement of primary thermometry with different experimental methods. The measure of this progress is illustrated by the remarkable reduction of the uncertainty associated with the determination of the physical properties which characterize a macroscopic system in thermal equilibrium at a particular thermodynamic temperature  $T$ . In fact, the energy  $kT/2$  associated with one degree of freedom of such a system can presently be estimated with a relative overall uncertainty of a few parts per million (ppm) using a variety of different techniques [1]. (Unless otherwise stated, all uncertainties in this work are standard uncertainties with coverage factor  $k = 1$  corresponding to a 68% confidence interval.) Most notably, in the case of acoustic gas thermometry (AGT), the relative uncertainty in the measurement of the internal kinetic energy of a dilute gas is lower than 1 ppm [2], competing with the precision achieved by the current temperature scale, the International Temperature Scale of 1990 (ITS-90) [3], based on the use of fixed points and platinum resistance thermometry.

Here, after reviewing the recent progress achieved in the development of several primary thermometry methods, we present some preliminary results obtained, mainly by AGT and dielectric constant gas thermometry (DCGT), in the determination of the differences  $(T - T_{90})$ , where  $T_{90}$  is the formal approximation to  $T$  determined from ITS-90 [3]. In particular, we consider whether recent measurements may resolve some inconsistencies in previous determinations [4], and prepare the ground for a future revised temperature scale, the so-called ITS-202x.

In the concluding section, we briefly discuss the perspectives and the future possibilities opened up by these research activities for primary thermometry and the dissemination of temperature standards.

## 2. Current activities in primary thermometry between 1 K and 1358 K

Working Group 4 (WG4) of the BIPM Consultative Committee of Thermometry recently completed a critical comparative review of the thermodynamic temperature measurements which constituted the backbone for the definition of ITS-90 [4]. Additionally, they considered more recent results (post the inception of the ITS-90) and highlighted some unexplained inconsistencies and the lack, or paucity, of supporting data in particular temperature ranges: notably between 25 K and 255 K; between 550 K and 690 K; and at the copper freezing point. These deficiencies ultimately limit the effectiveness of the dissemination of both the present and the future definition of the kelvin. In response to this recognized metrological need, a campaign of thermodynamic temperature measurements was organized within the framework of activities of the European Metrology Research Programme (EMRP) project denominated 'Implementing the new kelvin' (InK) [5]. Figure 1 graphically summarizes the temperature ranges covered by the InK project, by a number of different thermodynamic thermometry methods. These ranges were devised to extend beyond the previous applications of each method and to partially overlap with each other to favour the identification of possible sources of systematic error. Preliminary intermediate results and  $(T - T_{90})$  determinations obtained by these experiments recently became available and are discussed below.



**Figure 1.** Primary thermometry experiments being developed with different methods at various laboratories across the world. All these activities are organized by the joint research project denominated 'Implementing the new kelvin' under the coordination of the National Physical Laboratory (NPL). On the plot, the pattern of the shaded area refers to apparatus and measurement facilities being developed at different stages of the project [5]. The different institutes are co-authors of this paper except the National Institute of Metrology (NIM), China, the National Institute of Standards and Technology (NIST), USA, and the University of Valladolid (UVa), Spain. The key indicates where institutes expected to be with their primary thermometry measurements by month 24 (October 2014) and month 36 (October 2015) of the InK project. (Online version in colour.)

## (a) Gas thermometry

Constant volume gas thermometry (CVGT) has been the traditional method of primary thermometry over a wide intermediate temperature range. However, difficulties inherent to the accurate determination of extensive quantities like the volume of the measurement bulb or the actual amount of substance (gas) have limited the final attainable uncertainty of the method. This led to the development of other primary thermometry methods, based on the measurement of intensive quantities, in concert with some relevant theoretical or technological advance. Of particular note are the increased accuracy of first-principles calculation of material properties (e.g. the polarizability of He), the progress in electrical metrology instrumentation based on quantum standards and the development of improved optical sources and spectroscopic techniques. The discussion below summarizes the progress and the achievements of the primary thermometry methods which were most affected by these advances.

### (i) Acoustic gas thermometry

Kinetic theory and hydrodynamics provide a simple theoretical link, unaffected by relevant approximations, between the average speed of molecular motion and the speed of propagation of an acoustic signal through a dilute fluid [6]. This link was the basis for the development of a primary thermometry method based on the measurement of the speed of sound in helium, initially realized for use in the cryogenic range between 2 K and 20 K [7]. The aim of this early work was to avoid the many practical difficulties which limited the use of CVGT in the same temperature range. However, the potential of the acoustic method was only partially demonstrated by the acoustic technique of choice at that time, variable-pathlength interferometry with a cylindrical cavity. Indeed, this approach to AGT was still limited by its inherent technical difficulties and the incompleteness of the acoustic model [8]. Two decades after the initial proposal, primary AGT received new impulse, due to a substantial refinement of the theory and practice of spherical resonators [9] which led to a 10-fold improvement in the accuracy achievable in the determination of the speed of sound in a dilute monoatomic gas [10]. Following these

results, the strategy of using microwave resonances for the determination of the cavity thermal expansion further increased the accuracy of the technique [11], leading to several determinations of  $T$  in the overall temperature range between 7 K and 550 K showing unprecedented accuracy and mutual consistency [12–17].

Current research in the application of AGTs to primary thermometry aims at a further extension of its useful range to higher and lower temperatures and may finally cover an overall temperature range spanning between the  $\lambda$ -point of  $^4\text{He}$  at 2.2 K and the freezing point of copper at 1358 K. The achievement of this goal, while preserving the potential accuracy of AGT, presents a number of technical challenges, recently reviewed with a discussion of possible solutions [2]. At the lowest temperatures, i.e. below the temperature of the critical point of the measurement gases, significant perturbations may be induced from pre-condensation. These phenomena are not currently amenable to accurate modelling but their occurrence may be revealed by selective comparison of TM or TE microwave modes with a method previously exploited for microwave hygrometry [18]. At the highest temperatures, maintaining the gas purity within acceptable limits represents a critical issue, as does introducing the acoustic and microwave signals from transducers maintained at ambient temperature. The preliminary results obtained down to 7 K [15] and the recently demonstrated practicability of the acoustic/microwave technique up to the copper point [19,20] using test resonators with cylindrical symmetry represent promising advances towards the extension of the operating temperature range of AGT.

### (ii) Dielectric constant gas thermometry

The basic idea of DCGT is to replace the density usually accessed via extensive quantities (e.g. in CVGT) by the dielectric constant. Based on the validity of the Clausius–Mossotti equation, thermal energy can be determined from a permittivity and a pressure measurement in a fluid of known polarizability. For low-temperature primary thermometry, this method was first proposed and pursued with an experimental design based on a cylindrical capacitor [21], which is not substantially different from its successive developments, as recently reviewed [22]. However, the recent progress in the *ab initio* calculation of the polarizability of helium [23] has substantially increased the ultimate accuracy which may potentially be achieved by DCGT. Triggered by this advance, considerable progress has been made in the following areas, all required to facilitate accurate thermodynamic temperature measurement by the method: (i) pressure balances as primary pressure standards [24]; (ii) the instrumentation used for capacitance measurements [25]; and (iii) the characterization of the elastic properties of the materials used for the construction of the capacitors. Through these improvements, most of which have been made at the Physikalisch-Technische Bundesanstalt (PTB), increasingly accurate determinations of thermodynamic temperature in the low-temperature range have been made [26], and the most accurate, to date, determination of the Boltzmann constant at the triple point of water temperature  $T_{\text{TPW}}$  by this method [27].

Current work at PTB aims at a further reduction of the uncertainty of the DCGT method by testing the advantages inherent to the use of ring cross capacitors. Also, new determinations of  $(T - T_{90})$  will be pursued between 40 K and 200 K with different gases (He, Ne and Ar).

### (iii) Refractive index gas thermometry

Following the initial employment of microwave resonances to facilitate the dimensional characterization of cavities used for relative AGT, the supporting theory and the experimental practice of the microwave method to accurately determine the refractive index of gases have been substantially improved. Firstly, the technique was enhanced by the design of cavities with quasi-spherical geometry, allowing separation of the components of degenerate microwave resonances in order to make them more easily and precisely measurable [28]. Secondly, an analytical model was successfully derived to account for the perturbation induced by the quasi-spherical geometry [29] in the cavity eigenfrequencies. These notable advances suggested that the measurement of the refractive index of particular gases could lead to advances in primary metrology in both pressure

and temperature measurement. These developments, for example, have led to a demonstration of a helium-based primary pressure standard [30].

Although the strategy for exploiting these advances to develop a refractive index gas thermometer was outlined already in 2007 [28], no determinations of  $(T - T_{90})$  have yet been obtained by this method. However, primary thermometers based on this method are currently under development at the National Research Council of Canada [31] and are under consideration at the Laboratoire Commun de Métrologie (LNE-CNAM), and at the National Metrological Institutes of China (NIM) and of Italy (INRiM).

## (b) Solid-state and optical methods

### (i) Johnson noise thermometry

The metrological value of Johnson noise thermometry (JNT) resides in the purely electronic nature of its basic principle and measurement method, which provide an important independent check of the results obtained by gas-based primary thermometers. It may be interesting to note that the generalized validity of the fluctuation–dissipation theorem [32] holds for a variety of systems in thermal equilibrium, with analogues of the Johnson–Nyquist relation which describe the statistical fluctuations of the pressure or the electric or magnetic properties of a fluid. To our knowledge, no practical experiment based on these principles has yet been proposed or implemented to achieve a direct metrological characterization of the energy content of such states. However, the density fluctuations in a fluid medium are the main contributor to elastic scattering of light at ordinary wavelengths, which is the basic principle of Rayleigh scattering primary thermometry [33,34].

The details of the historical progress and achievements obtained by JNT have been recently reviewed [35,36]. It will suffice to remark here that a benchmark in this progress, recently leading to a determination of the Boltzmann constant with an overall uncertainty of only 3.9 ppm [36], was achieved through the development, at the National Institute of Standards and Technology (NIST), of precisely calculable noise sources based on quantum standards [37]. Also, the increase in measurement bandwidth has led to a significant reduction of the integration time needed for the accurate implementation of the method. The integration time required for the measurement above [36] was 31 days, which places JNT on the verge of being a practical method for the realization of primary temperature standards. Previous application of JNT in the determination of  $(T - T_{90})$  was achieved, by operation in relative or absolute mode, at the freezing points of Sn (505 K) and Zn (693 K) [38]. Current work is ongoing in cooperation between NIST and NIM to extend the potential of these recent advances and achieve  $(T - T_{90})$  determinations over a wider temperature range. At the highest temperatures, suppressing the electromagnetic interference from heat sources surrounding the experiment may represent a critical issue.

### (ii) Doppler broadening

High-resolution laser absorption spectrometry, in the linear regime of radiation–matter interaction, allows observation of the shape of atomic or molecular transitions between a pair of quantum states, with extraordinary fidelity. In the Doppler regime, when the mean free path of the absorbers is much larger than the optical wavelength, the width of a spectral line for a gas at thermodynamic equilibrium is mostly influenced by the thermal motion of the atomic or molecular constituents. The so-called Doppler width, which is due to the Doppler effect, represents a powerful tool to link the thermal energy to an optical frequency. This is the basis of a relatively new method of primary gas thermometry, known as Doppler broadening thermometry (DBT) [39]. This methodology is currently at the stage of further development and optimization in a few specialized laboratories, worldwide.

The main issue currently limiting the DBT accuracy is due to line-shape modelling. Even in the Doppler regime, the absorption profile is perturbed by binary collisions that lead to an additional broadening of the spectral line. Furthermore, depending on the experimental precision,

narrowing effects can be observed, typically due to the joint occurrence of two phenomena: the speed dependence of collision relaxation rates and the averaging effect of velocity-changing collisions. A fully quantum-mechanical treatment of spectral line shapes is very complicated, especially for self-colliding polyatomic molecules. Despite that, recent progress of modelling capabilities, even though in a semi-classical framework, has been one of the key elements leading to the recent achievements obtained by DBT [40]. So far, the best DBT implementation has been performed on  $\text{H}_2^{18}\text{O}$  molecules, using a dual laser approach at a wavelength of  $1.4\ \mu\text{m}$  [41]. This sophisticated apparatus, as developed at the Second University of Naples, made it possible to measure the Boltzmann constant with a combined uncertainty of 24 parts in  $10^6$  [42]. More recently, the first  $(T - T_{90})$  determinations were demonstrated in the temperature interval between the triple point of water and the melting point of gallium  $T_{\text{Ga}}$ . As an example of the preliminary results which are being achieved, the statistical analysis of 100 spectra determined  $T_{\text{Ga}} = 302.82(5)\ \text{K}$ .

Current efforts towards a reduction of the overall uncertainty concentrate on statistical issues and the systematic error associated with the choice of the line-shape model. Recently, a global fitting approach has been developed for the simultaneous analysis of a number of spectra recorded at different pressures, sharing a restricted number of free parameters, including the Doppler width [43]. This approach has the important advantage that it reduces correlations between model parameters. Furthermore, alternative experimental configurations are being planned with two different test gases (e.g.  $\text{C}_2\text{H}_2$  and  $\text{H}_2^{18}\text{O}$ ) maintained at the same temperature within a single absorption cell, a circumstance that will place a severe physical constraint on the thermal energy, favouring a significant reduction of the measurement uncertainty by the identification of possible systematics. A recent updated review of the current status of DBT is given in [44].

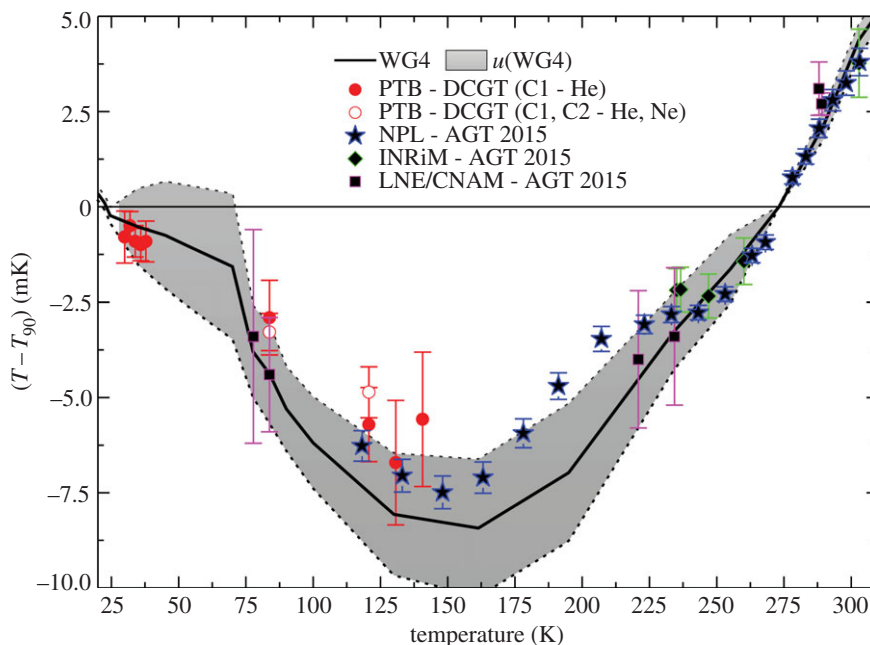
### 3. Discussion of recent results<sup>1</sup>

Figure 2 shows the recent determinations of  $(T - T_{90})$  obtained by various laboratories with two different primary thermometry methods. These are, namely, DCGT measurements at PTB, in the range between 29 K and 140 K, and AGT measurements at LNE-CNAM, INRIM and NPL, in the overall range between 78 K and 303 K.

The salient features of each experiment can be summarized as follows:

- The recent measurements performed at PTB extend the useful operating range of the DCGT experiment to higher temperatures [45]. In pursuing the new results, particular care was taken to check for possible systematic sources of uncertainty, by repeating two isotherms (at 84 K and 121 K) employing two different capacitors, and using both He and Ne as the measurement gases. Remarkably, the results obtained from all these combinations were found to be consistent with each other. Also, the overall uncertainty was reduced owing to significant improvements of the methods used to determine the compressibility of the capacitors as a function of temperature, leading to a correction of previous results in the temperature range between 2.5 K and 36 K [26].
- The AGT apparatus used at NPL is based on the resonator previously characterized for an extremely accurate determination of the Boltzmann constant  $k$  [46] with multiple modifications to the thermostating system to cover the overall temperature range between 118 K and 303 K. The AGT was operated in relative mode, with measurements of the speed of sound in Ar recorded as a function of pressure along several (20) closely spaced isotherms, including  $T_{\text{TPW}}$ . For this experiment, a detailed description of the separate uncertainty contributions to the determinations of  $T$  and  $T_{90}$ , and a critical discussion of the results, may be found elsewhere [47].

<sup>1</sup>All the thermodynamic temperature results which are discussed and displayed in this section must be considered preliminary and subject to possible future variations, as their final evaluation is currently being completed, and will be the subject of future publications.

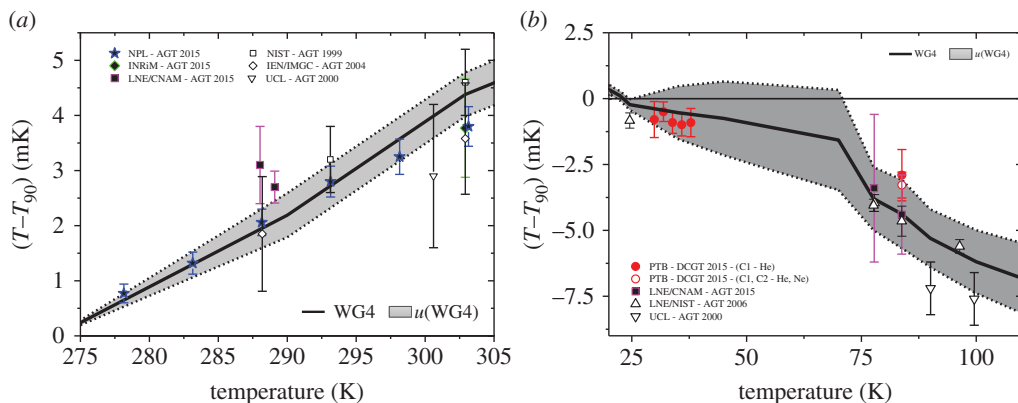


**Figure 2.** Comparison of recent determinations of the differences  $(T - T_{90})$  by DCGT and AGT. The black line and the shaded area display the best fit and the uncertainty of an interpolation of previous  $(T - T_{90})$  data by CCT Working Group 4 [4]. (Online version in colour.)

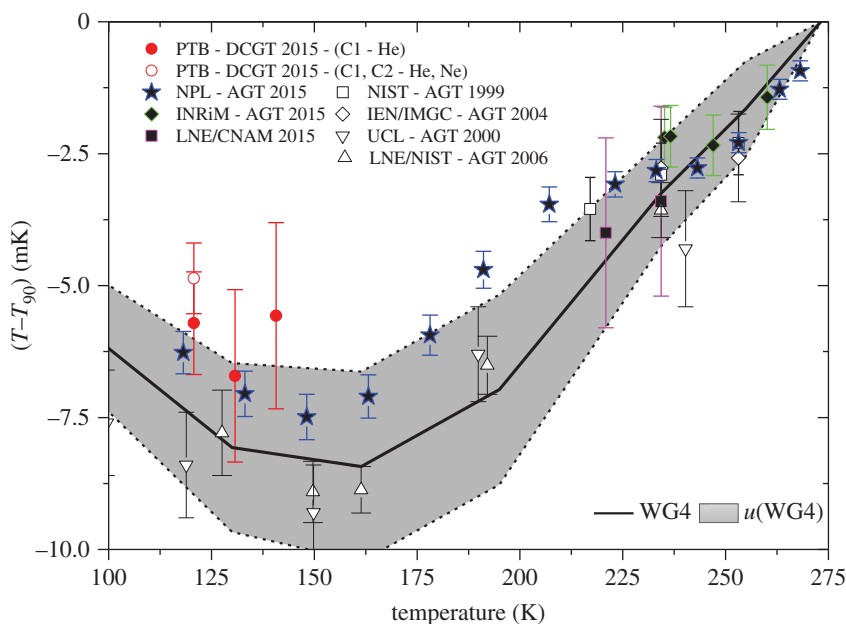
- LNE-CNAM has designed and is currently developing a variety of apparatus and cryostats to conduct AGT experiments over the wide temperature range between 4 K and 350 K. At present, results obtained using the small volume (0.5 litre) resonator previously used for an accurate determination of  $k$  [48] and a larger volume (3.1 litre) resonator were reported at six temperatures between 77 K and 290 K [49]. The values and the rather large corresponding uncertainties displayed for these results in figure 2 should be considered provisional and are going to be significantly reduced when the calibration of the standard thermometers used in the experiments, which are currently ongoing, will be completed, providing a reliable linkage to ITS-90.
- The AGT apparatus previously used at INRiM to achieve a precise determination of  $k$  [50], without any relevant modifications, operated in the temperature range between 235 K and 303 K, led to the measurements of  $(T - T_{90})$  displayed in figure 2, using helium as the test gas [51].

As a whole, these results are mostly consistent with previous  $(T - T_{90})$  determinations obtained with the same technique, where available, and with the WG4 interpolation [4]. This is particularly true for the range above  $T_{TPW}$  up to  $T_{Ca}$  and the temperature range below 100 K, separately displayed with more detail in figure 3 to ease comparison with older data. Particularly, the mutual consistency of various AGT data at  $T_{Ca}$  is indeed striking, considering that these data were obtained with rather different, weakly correlated experiments [52], and motivates the further development of AGT at a higher temperature range. Below 100 K, the new DCGT results of PTB are in satisfactory agreement with the new and previous AGT results of LNE/NIST. A similarly satisfactory agreement of new DCGT results is found between 120 K and 140 K (figure 4) with new AGT results obtained at NPL.

Considering the intermediate range between 100 K and  $T_{TPW}$  (figure 4), we note that the new results are mostly consistent with the WG4 interpolation. Particularly, below the triple point of mercury at 234 K, both the new DCGT data of PTB [45] and the AGT data of NPL [47] indicate



**Figure 3.** (a) Comparison of AGT determinations of  $(T - T_{90})$  above 273.16 K. (b) Comparison of determinations of  $(T - T_{90})$  by DCGT and AGT between 20 K and 100 K. (Online version in colour.)



**Figure 4.** Comparison of  $(T - T_{90})$  determinations by DCGT and AGT between 100 K and 273.16 K. (Online version in colour.)

that the magnitude of the differences  $(T - T_{90})$  have a smaller (less negative) magnitude than previously determined by AGT [13,17], in slightly better agreement with the CVGT data of Kemp *et al.* [53] than with those of Astrov *et al.* [54].

Most importantly, the outstanding progress achieved by the AGT method during the last few years is well illustrated by the visual comparison of the uncertainty of the WG4 interpolation (shaded area in figure 4) with the much smaller uncertainty associated with the dense NPL dataset. By separating the contributions to the overall uncertainty of  $(T - T_{90})$  of [47], it is evident that the uncertainty associated with the acoustic determination of  $T$  is significantly smaller than the total uncertainty which can be achieved in the realization of ITS-90 using standard platinum resistance thermometers [55]. In fact, the unprecedented precision and accuracy of NPL thermometry reveals some subtle features of the differences  $(T - T_{90})$ , previously unnoticed, and whose origin is likely to be inherent in the reference function of the ITS-90. Moreover, analysis of NPL data close to  $T_{TPW}$  sheds new light on the previously discussed [56] discontinuity of the



slope  $d(T - T_{90})/dT_{90}$ . Estimating the slope  $d(T - T_{90})/dT_{90}$  above  $T_{TPW}$  from  $(T - T_{90})$  at the gallium point gives a good estimate of the slope just above  $T_{TPW}$ . However, estimating the slope  $d(T - T_{90})/dT_{90}$  below  $T_{TPW}$  from  $(T - T_{90})$  at the mercury point gives a misleading estimate of the slope just below  $T_{TPW}$ . The discontinuity (defined as the slope above  $T_{TPW}$  minus the slope below  $T_{TPW}$ ) appears to be slightly negative or possibly zero ( $-0.02 \pm 0.02 \text{ mK K}^{-1}$ ) rather than the previously reported [4] positive values ( $+0.03 \text{ mK K}^{-1}$ ).

## 4. Outlook

With the exception of the first internationally agreed temperature scale (ITS), which was based on gas thermometry with hydrogen, ITSs in their successive versions have since, from ITS-27 on, been based on the selection of a number of defined fixed points and interpolating instruments and equations. The main justification for this choice is the need to enhance the reproducibility and practical convenience of calibration procedures. Such practice has required continuous refinement of the interpolating equations and the temperatures assigned to the fixed points to reduce the deviation from thermodynamic temperature measured by primary thermometers, as increasingly more accurate versions of such instruments became available. This well-established practice may change in the near future, as the foreseen new definition of the kelvin will take place and because the technology of primary thermometry with different methods has evolved to the point that the accuracy in the determination of the thermodynamic temperature  $T$  challenges the overall uncertainty in the realization of ITS-90. This, for example, has already been proposed and the framework put in place for high-temperature primary thermometry, by primary radiometry above the silver point [57].

The current research activities in primary thermometry aim at accurate and consistent determinations of the differences  $(T - T_{90})$  by different primary thermometry methods over increasingly wide temperature ranges. If these activities prove successful, it is likely that they may finally bring about a substantial simplification of the primary methods, as needed to compete with the traditional dissemination techniques based on fixed points, whose practicality is currently unrivalled. If achieved, such advances will naturally lead to a direct dissemination of the thermodynamic temperature, traceable directly to the new kelvin definition [58]. This would in turn significantly reduce or even, in the longer term, eliminate the need for a practical scale.

**Authors' contributions.** All authors contributed to the design, the realization and the operation of primary thermometry experiments at various laboratories. All authors contributed to the final version of the manuscript.

**Competing interests.** We declare we have no competing interests.

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