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Platinum resistivity below 273.16 K: a tale of two reference functions

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Abstract

Four platinum resistance thermometer data sets of resistance ratio as a function of temperature from 13.8033 K to 273.16 K are fitted to two different functions. One has the form of the ITS-90 reference function (the “Kemp model”) while the second is the mathematically more complex model of Nicholas. Both are shown to fit the resistivity data well, though the residuals for the Kemp model are lower. Both models also cope well with adjustments to the input temperatures consistent with the most recent consensus estimates of $T-T_{90}$. There is no evidence from the work reported herein that either of the models is useful as an arbiter of thermodynamic temperature data.

1. Introduction

The temperature dependence of platinum resistivity has been fundamental to the International Temperature Scale since its inception in 1927. Though the platinum wires from which individual thermometers are fabricated differ from one another in the concentration and nature of their residual chemical impurities and in their specific physical imperfections (i.e. the number and concentration of lattice defects – grain boundaries, vacancies, dislocations, etc.), the overall behaviour of PRTs acceptable as scale interpolating devices is broadly similar.

From 13.8033 K to 1234.93 K, the International Temperature Scale of 1990 (ITS-90) “is defined by means of a platinum resistance thermometer (PRT) calibrated at specified sets of defining fixed points, and using specified reference and deviation functions for interpolation at intervening temperatures” [1]. ITS-90 relies on two reference functions to describe the resistivity of a PRT with respect to its value at 273.16 K (the resistance ratio, W): one for the range from 13.8033 K to 273.16 K and the second from 273.15 K to 1234.93 K. The development of the former is described by Kemp [2], and subsequent discussion here will focus exclusively on the range below 273.16 K. The resistance ratio defined by the reference function is referred to as $W_r(T_{90})$. Below 273.16 K, it is defined by the equation,

$$\ln[W_r(T_{90})] = A_0 + \sum_{i=1}^{12} A_i \left[\frac{\ln(T_{90}/273.16) + 1.5}{1.5} \right]^i \quad (1)$$

Kemp obtained the 13 coefficients by fitting W versus temperature data for PRT 217894 from the Ward and Compton [3] data set (which reported temperatures on IPTS-68), but

adjusted the Ward and Compton temperatures to take into account the consensus estimate of $T-T_{68}$ (effectively $T_{90}-T_{68}$) at the time the ITS-90 was formulated. (Here the symbol T denotes “true” (i.e. thermodynamic) temperatures.) Kemp shows [2] that the residuals with respect to his fit do not exceed $\pm 3 \times 10^{-6}$ in W .

The title of this paper speaks of two reference functions, and thus far only one has been described. In 1992, Nicholas presented [4] an alternative expression that combines two 3rd-order Debye functions with an Einstein function to describe platinum resistivity. The equation takes the form

$$W(T) = a_0 + a_1 T D_3[\Theta_1(T)/T] - a_2 T D_3[\Theta_2(T)/T] + a_3 / \{\exp[\Theta_3(T)/T] - 1\} \quad (2)$$

where

$$\Theta_1(T) = \Theta_1(1 + b_1/T + c_1/T^2) \quad (3)$$

$$\Theta_2(T) = \Theta_2(1 + b_2/T + c_2/T^2) \quad (4)$$

$$\Theta_3(T) = \Theta_3(1 + b_3/T) \quad (5)$$

$$D_3(x) = \frac{1}{x^3} \int_0^x \frac{t^3 dt}{\exp(t) - 1} \quad (6)$$

The Nicholas model described above has 12 coefficients and its form requires that nonlinear fitting techniques be employed. Later [5], Nicholas reduced the number of parameters to 9 by setting $a_1 = 2a_2$ and replacing the last term in (2) by

$$a_3 \{1 / [\exp(\Theta_3/T) - 1] + 2 / [\exp(\Theta_3/T) - 1]^2\} \quad (7)$$

with $\Theta_3 = 1565.1$ K. However, in the analysis that follows, Nicholas’ original version (equations (2) to (6)) will be used.

2. Testing the model equations

One means to test the utility of (1) and (2) is to examine how well they fit the experimental data. When using (1) to fit various PRT data sets, it will be referred to it as “the Kemp model” to avoid confusion with the ITS-90 reference function, $W_r(T_{90})$, which has specific values for the coefficients defined by the text of the ITS-90 [1].

Four data sets have been used to test the Kemp and Nicholas models. The same data sets were used [6] to explore the non-uniqueness of the ITS-90. They include the Ward and Compton data [3], the EUROMET comparison of capsule-style PRTs [7], comparison data collected during the CCT-K2 comparison [8], and comparison data collected at NRC and reported in 2002 [6] supplemented by original data that has not been previously published (NRC 2002). The data sets comprise 35, 11, 8, and 14 thermometers, respectively. The NRC 2002 data consists of 2 comparison runs of 8 thermometers, with 2 thermometers common to the two sets.

2.1 Kemp model – linear least squares

Some years ago, in an effort [9] aimed at removing the slope discontinuity in the ITS-90 at 273.16 K, the data underlying the ITS-90 reference function was altered slightly and refitted using a FORTRAN program that implements the singular value decomposition technique [10] to deal with the near-singular matrix that results when applying the Kemp model to the PRT data. For the current analysis, the MATLAB Curve Fitting Toolbox [11] was employed. To distribute the residuals more evenly across the temperature range, the weights in the fit were set equal to W . The four data sets were fitted without difficulty, with the residuals as shown in figures 1-4. The vertical axis is expressed in units of resistance ratio (W), and is therefore dimensionless. Above 50 K, the sensitivity dW_r/dT is approximately $4 \times 10^{-6} \text{ mK}^{-1}$ and therefore we see that in all cases the residuals above 50 K are less than 1 mK. Below 50 K, the sensitivity declines rapidly and it is best to undertake the required computations to obtain the deviations in terms of temperature. The residuals remain below 1 mK for most, but not all, thermometers as the sensitivity approaches $2.4 \times 10^{-7} \text{ mK}^{-1}$ at the lowest temperatures of the comparison.

Figure 1. The residuals obtained when fitting the Ward and Compton data with the Kemp model.

Figure 2. The residuals obtained when fitting the EUROMET data with the Kemp model.

Figure 3. The residuals obtained when fitting the CCT-K2 data with the Kemp model.

Figure 4. The residuals obtained when fitting the NRC 2002 data with the Kemp model.

2.2 Nicholas model – nonlinear least squares

The nonlinear least squares fitting procedure for the Nicholas model also made use of the MATLAB Curve Fitting Toolbox [11]. In this case, the data were unweighted. The nonlinear fitting procedure requires starting values for the coefficients and the process proceeds iteratively until either a specified tolerance is reached or the maximum iterations are completed. The fitting procedure requires greater computational time compared to the linear least squares procedure applicable to the Kemp model. While satisfactory fits were obtained for the majority of the PRTs, the residuals for some of the thermometers exceed the somewhat arbitrary bounds $\pm 8 \times 10^{-6}$ and these have been omitted (as noted) from the figures 5-8 summarizing the results. Altering the initial values for the fitting procedure may allow better fits to the excluded thermometers, but one of the goals was to assess the ease and universality of the fitting when applied to groups of thermometers. The deviations, especially in figures 6-8, clearly display structure though the scatter among the various thermometers is small, suggesting that the model could be improved to better represent the data. The peak-to-peak residuals exceed those of the Kemp model in all cases.

Examination of the W -values (by plotting $W - W_r$) of the excluded thermometers shows that, in many cases, those excluded from figures 5-8 have the largest deviations from W_r . This is the case for PRTs 223695 and B264 excluded from figure 6, PRT 223695 excluded from figure 7, and PRTs 1158062 and 1158062 excluded from figure 8. For these PRTs, the maximum $W - W_r$ values range from $\sim 4 \times 10^{-4}$ to $\sim 7 \times 10^{-4}$. PRT 188682 has the highest $W - W_r$ ($\sim 5 \times 10^{-4}$) within the Ward and Compton data set and was a borderline case for exclusion, but was not. However, PRT 43 was excluded from figure 5 even though its

maximum $W - W_r$ is only $\sim 1.4 \times 10^{-4}$, so this criterion by itself is not necessarily a predictor of difficulty for the Nicholas model. In addition, the Ward and Compton data set includes PRTs 1158062 and 1158066, both of which were excluded from figure 8 but adequately fitted and included within figure 5. Evidently, the number and placement of data points (and perhaps other factors) influences the success or failure of the fitting procedure. Nonetheless, the fact that PRT 223695 was omitted from both figures 6 and 7 suggests that there is something intrinsic in its behaviour that challenged the model.

Figure 5. The residuals obtained when fitting the Ward and Compton data with the Nicholas model. Thermometer 43 has been omitted from the graph.

Figure 6. The residuals obtained when fitting the EUROMET data with the Nicholas model. Thermometers 223695 and B264 have been omitted from the graph.

Figure 7. The residuals obtained when fitting the CCT-K2 data with the Nicholas model. Thermometers 1886906 and 223695 have been omitted from the graph.

Figure 8. The residuals obtained when fitting the NRC 2002 data with the Nicholas model. Thermometers 1158062 and 1158066 have been omitted from the graph.

3. Discussion

We have shown that both the Kemp model and the Nicholas model are able to represent the behaviour of platinum resistivity at the millikelvin level, though the Kemp model achieves lower residuals with less mathematical complexity that is amenable to an efficient linear least squares fitting procedure as opposed to the nonlinear least squares methodology required by the Nicholas model.

In addition to the analysis presented in the preceding section, additional computations were made after altering the temperatures of the data sets to take into account the most recent recommendation from the Consultative Committee for Thermometry's Working Group 4 for $T - T_{90}$ [12]:

$$(T - T_{90}) / \text{mK} = \sum_{i=0}^7 b_i (\log_{10}(T_{90} / T_{\text{TPW}}))^{i+1} \quad (8)$$

with coefficients $b_0 = 4.42457 \times 10^1$, $b_1 = -1.76311 \times 10^2$, $b_2 = -1.53985 \times 10^3$, $b_3 = -3.63685 \times 10^3$, $b_4 = -4.19898 \times 10^3$, $b_5 = -2.61319 \times 10^3$, $b_6 = -8.41922 \times 10^2$, and $b_7 = -1.10322 \times 10^2$. Because these changes made little or no discernible difference to the quality of the fits for both the Kemp and Nicholas models, graphs of the resulting residuals are not included herein due to their similarity to figures 1-8. Table 1 lists the coefficients obtained by fitting the adjusted temperatures for PRT 217894, the thermometer on which the ITS-90 reference function is based. A refitting of the data for this PRT (or perhaps a

different one more representative of the “average” behaviour) with temperatures adjusted to accord with the best estimate of thermodynamic temperature could offer a means to update the coefficients of the ITS reference function. Such an updating of the coefficients of the reference function, combined with revised temperatures for the defining fixed points, could provide the *Mise en pratique* for the definition of the kelvin [13] with a mechanism to bring the International Temperature Scale into accord with contemporary estimates of thermodynamic temperature while retaining the mathematical structure of the ITS-90.

In his 1995 paper, Nicholas [5] shows fitting residuals with peak-to-peak deviations that exceed 10 mK for 6 thermometers. The differences among the thermometers are very small and there is clearly a systematic difference between his model equation (T_{fit}) and the ITS-90 (T_{90}). Nicholas tried various weighting schemes and suggested that, with a low weighting of the data in the range 70 K to 270 K, his model showed better agreement with the “new” (at the time) acoustic thermometry results that deviate from the ITS-90 by as much as 10 mK near 150 K. By testing both the Kemp and Nicholas models with the most recent consensus estimates of $T-T_{90}$ (that approach 9 mK near 150 K), we have found no evidence that either the Kemp or Nicholas models can be used as arbiters of thermodynamic temperature data (as Nicholas suggested) when fitting PRT data within the range 13.8 K to 273.16 K.

Table 1. Coefficients for the Kemp model applied to PRT 217894. The final column lists the coefficients obtained when the temperatures given by Kemp [2] are adjusted to take into account the most recent consensus estimates of $T-T_{90}$ [12].

	ITS-90	“revised”
A_0	−2.135 347 29	−2.135 287 06
A_1	3.183 247 20	3.183 373 45
A_2	−1.801 435 97	−1.801 510 59
A_3	0.717 272 04	0.716 922 15
A_4	0.503 440 27	0.504 590 04
A_5	−0.618 993 95	−0.618 560 20
A_6	−0.053 323 22	−0.058 806 44
A_7	0.280 213 62	0.280 154 48
A_8	0.107 152 24	0.116 394 40
A_9	−0.293 028 65	−0.293 013 83
A_{10}	0.044 598 72	0.037 660 11
A_{11}	0.118 686 32	0.118 568 17
A_{12}	−0.052 481 34	−0.050 486 87

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