The discontinuity in T_{90} at the triple point of water

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Summary

- The discontinuity in the first derivative of T_{90} at the triple point of water is a real effect.
- The discontinuity arises from (i) the inconsistency of the reference resistance ratios, W_r, assigned to the fixed points by ITS-90, and (ii) the termination of the ITS-90 sub-ranges at 0.01 ºC.
- The inconsistency in the assigned W_r values above and below 0.01 ºC is an artefact of ITS-90 being based on two different SPRTs.
- The mathematics of the slope discontinuity is similar to that for subrange inconsistency because they have the same root cause.
- Because the first derivative of the interpolating equations is different for every interpolation, the discontinuity does not have a single well-defined value.
- In principle we could adjust some of the W_r values so that the average discontinuity is zero.

1. Mathematical origin of the discontinuity

Many attributes are required of a practical temperature scale like ITS-90, including continuity, thermodynamic accuracy, continuity of the first derivative, and thermodynamic accuracy of the first derivative. The latter two properties are required to ensure sensible measurements of thermophysical properties such as heat capacity, either for constant volume or constant pressure:

$$c_v = \left(\frac{\partial U}{\partial T}\right)_v \text{ or } c_p = \left(\frac{\partial U}{\partial T}\right)_p . \tag{1}$$

In practice measurements are usually made with respect to ITS-90, so it is implicitly assumed that,

$$\left(\frac{\partial U}{\partial T}\right) = \left(\frac{\partial U}{\partial T_{90}}\right). \tag{2}$$

Thus thermodynamic accuracy of the first derivative of scale temperature is required to ensure accuracy of the measurement of heat capacity (and other properties). Continuity of the first derivative is necessary to ensure that glitches in ITS-90 are not mistaken for phase transitions in the material under test.

By analogy with the our assessments of $T - T_{90}$ we (CCT-WG4) should therefore assess

$$\frac{\partial T}{\partial T} - \frac{\partial T_{90}}{\partial T} = 1 - \frac{\partial T_{90}}{\partial T} . \tag{3}$$

Direct measurements of $\partial T_{90} / \partial T$ prove to be too insensitive to be practical but we can break the problem down and recognise and measure contributions to $\partial T_{90} / \partial T$:

$$\frac{\partial T_{90}}{\partial T} = \frac{\partial T_{90}}{\partial W_\mathrm{r}} \times \frac{\partial W_\mathrm{r}}{\partial W} \times \frac{\partial W}{\partial T} . \tag{4}$$

The first term of (4) is simply the derivative of the reference function defined by ITS-90. By design this function has a continuous first derivative so cannot be the source of any discontinuity.

The second term of (4) is the derivative of an ITS-90 interpolating function. While all of these functions are demonstrably continuous within their respective subranges, discontinuities occur where subranges terminate, especially at the triple point of water where all, but one, of the subranges terminate. Note that there is no discontinuity at the water triple point if the mercury-gallium subrange is used.

The third term of (4) is proportional to $\partial R / \partial T$, which is an explicit and individual property of an SPRT. We also assume this to be continuous in the first derivative, and certainly it is very unlikely for such a discontinuity to occur at 0.01 ºC. (Does anyone know of reports of discontinuities in $\partial R / \partial T$?) The $\partial R / \partial T$ is different for every SPRT, and ideally the interpolations compensate for the different sensitivities of different SPRTs so that (4) is very close to unity everywhere.

The observation that the cause of the discontinuity lies within the ITS-90 $W_r(W)$ interpolations can be expanded. If the slopes of the two neighbouring interpolations are the same where one or both interpolations terminate, then evidently there is no discontinuity. This shows that the discontinuity phenomenon shares features with subrange inconsistency (SRI): SRI is the difference between two interpolations operating over the same temperature range. The slope discontinuity arises as the difference between the derivatives of interpolations operating over neighbouring subranges.

2. Summary of observations on SRI

Recently Greg Strouse and I published a paper on the subrange inconsistency (SRI) in ITS-90 [1]. In the mathematical analysis of the equations for the SRI, one parameter, which we labelled as S_i, kept recurring in the equations:

$$S_i = \frac{W_i - 1}{W_{r,i} - 1} \tag{5}$$

where W_i is the measured fixed-point resistance ratio for an SPRT at the i^{th} fixed point (i = Hg, Ar, Ga, Sn, …) , and $W_{r,i}$ is the reference resistance ratio for the same fixed point. The S_i value is the ratio of the sensitivity of the SPRT under test to that of the SPRT used to define ITS-90, i.e.,

$$S_i = \left[\frac{\Delta W_i}{\Delta T}\right]\left[\frac{\Delta W_{r,i}}{\Delta T}\right]^{-1}. \tag{6}$$

SPRTs with the highest S_i values are usually considered to be the highest grade.

Figure 1 below plots the S_i values for a total of 60 different SPRTs at the Ar, Hg, Sn, Zn, Al, and Ag fixed points. Plots of the S_i values, such as Figure 1, are very useful for assessing the quality of an SPRT and the consistency of a set of fixed-point measurements. Also, we can draw the following observations:

(1) All of the mathematical expressions for SRI are in terms of differences in the S_i values. For example, the SRI for the water-zinc and water-tin subranges is

$$^{\mathrm{Zn}}W_r(W) - {}^{\mathrm{Sn}}W_r(W) = \frac{(W-1)(W-W_{\mathrm{Sn}})}{(W_{\mathrm{In}}-W_{\mathrm{Sn}})(W_{\mathrm{Zn}}-W_{\mathrm{Sn}})} \times \left(W_{\mathrm{Zn}}\left[\frac{1}{S_{\mathrm{Sn}}} - \frac{1}{S_{\mathrm{In}}}\right] + W_{\mathrm{Sn}}\left[\frac{1}{S_{\mathrm{In}}} - \frac{1}{S_{\mathrm{Zn}}}\right] + W_{\mathrm{In}}\left[\frac{1}{S_{\mathrm{Zn}}} - \frac{1}{S_{\mathrm{In}}}\right]\right). \tag{7}$$

If all the S_i values are the same then there is no SRI.

(2) A horizontal line for a single SPRT on Figure 1 comes about because the differences in SPRTs behaviour are determined almost entirely by Matthiessen's rule, so that a linear interpolation is sufficient. Most of the SPRTs close to S_i = 1 exhibit this behaviour, and therefore have a low SRI.

(3) SPRTs for which the 1/S values lie on a straight line that is not horizontal will have zero SRI for all interpolating equations that are quadratic or higher order. SPRTs of poorer quality (low S_i value) all show a trend for falling S_i values with increasing temperature and therefore require, as a minimum, quadratic interpolation.

(4) One of the most conspicuous features of Figure 1 is the consistent drop in S_i values between the mercury point and tin point. This feature would be more apparent if gallium and indium fixed-point data were included. The difference between sets of S_i values above and below 0.01 ºC is the cause of the magnitude of the discontinuity observed by Dr Rusby and others at the triple point of water. The root cause is the use of two different thermometers, a capsule thermometer below 0.01 ºC and a HTSPRT above 0.01 ºC, to determine the W_r values to the used in ITS-90. The two thermometers were not sufficiently similar to avoid the creation of the discontinuity.

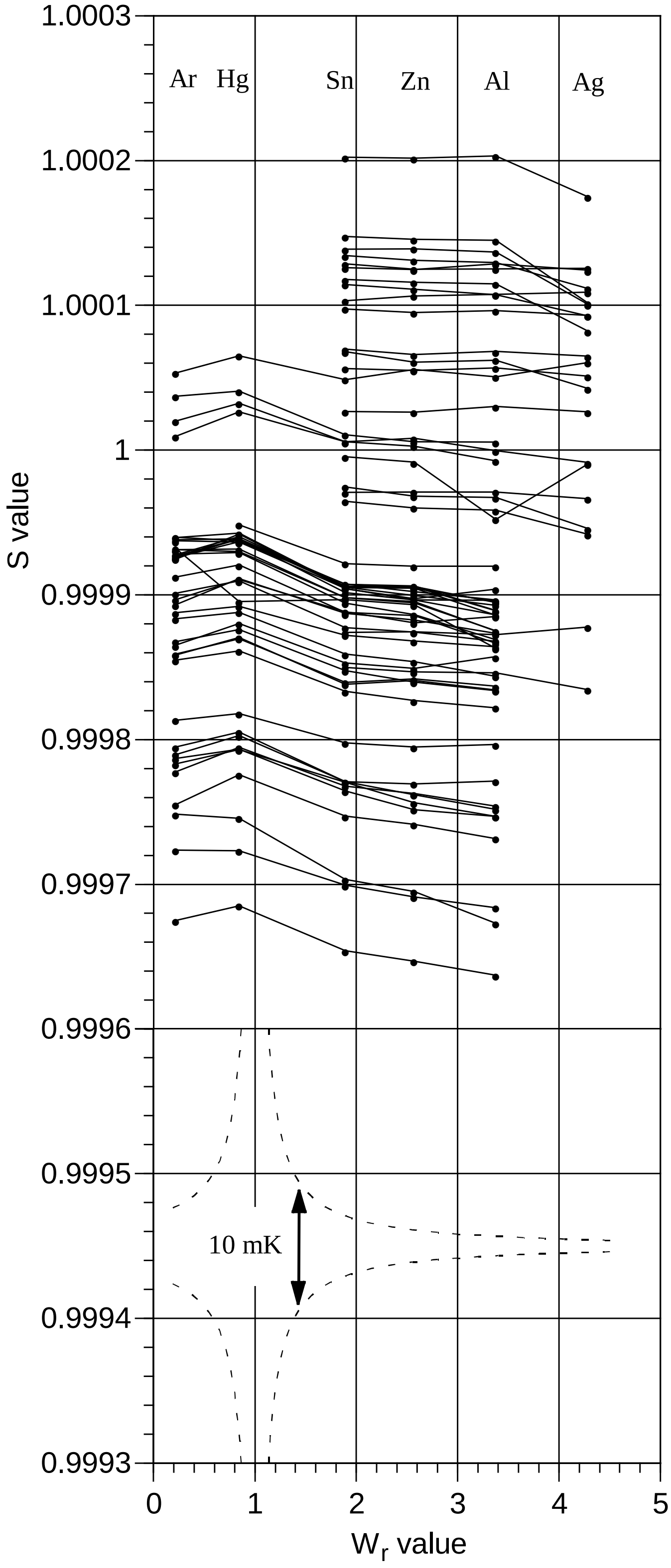

Figure 1: The ratio $S_i = (W_i - 1)/(W_{r,i} - 1)$ for 60 SPRTs measured at fixed points in the range from argon to silver. The dotted curves at the bottom of the graph indicate the sensitivity of S_i values to changes in the fixed-point temperatures. The ITS-90 qualification criteria for SPRTs correspond to $S_i > 0.9994$.

3. Examples of expressions for the discontinuity

All of the ITS-90 SPRT interpolating equations can be written in the form

$$W_{\mathrm{r}}(W) = \sum_{i=1}^{N} W_{\mathrm{r},i}\, f_i(W; W_2, ..., W_N) \ . \tag{8}$$

where $W_{\mathrm{r},i}$, are the reference resistance ratios assigned by ITS-90 to the N fixed points used in the interpolation, and the $f_i(W)$, are functions of measured resistance ratios only. In (8), the various fixed points and interpolating functions are enumerated by the index i, and the W_i values are the values measured at the fixed points. The index may be numeric or the chemical symbol for the corresponding fixed-point substance. In all cases where numeric indices are used, $i = 1$ corresponds to the water triple point. As shown in [1], the interpolating equations can also be written in the form

$$W_{\mathrm{r}}(W) - 1 = \sum_{i=2}^{N} (W_{\mathrm{r},i} - 1)\, f_i(W) \ . \tag{9}$$

which greatly simplified the analysis of SRI in ITS-90, and simplifies the calculation of the difference in slopes here. For example, the linear interpolation for the water-indium subrange can be rewritten as:

$${}^{\mathrm{In}}W_{\mathrm{r}}(W) - 1 = (W-1)\frac{\left(W_{\mathrm{r,In}} - 1\right)}{(W_{\mathrm{In}} - 1)} \ . \tag{10}$$

The derivative at W =1 is given by

$$\frac{d\,{}^{\mathrm{In}}W_{\mathrm{r}}}{dW} = \frac{W_{\mathrm{r,In}} - 1}{W_{\mathrm{In}} - 1} = \frac{1}{S_{\mathrm{In}}} \tag{11}$$

so that the slope of the water-indium interpolation is the $1/S_i$ value measured at the indium point. Following the same line of reasoning, any linear interpolating equation corresponds to S = constant in Figure 1, and the difference in slopes is the difference in the 1/S values when extrapolated to W = 1. Thus, the slope of the water-gallium interpolation is $1/S_{\mathrm{Ga}}$, and the difference between the slopes for a linear gallium and linear indium interpolation is $1/S_{\mathrm{Ga}} - 1/S_{\mathrm{In}}$.

The interpolating equation for the water-tin subrange is

$$\begin{aligned} {}^{\mathrm{Sn}}W_{\mathrm{r}}(W) - 1 &= (W-1)\frac{(W - W_{\mathrm{Sn}})}{(W_{\mathrm{In}} - W_{\mathrm{Sn}})}\frac{\left(W_{\mathrm{r,In}} - 1\right)}{(W_{\mathrm{In}} - 1)} + (W-1)\frac{(W - W_{\mathrm{In}})}{(W_{\mathrm{Sn}} - W_{\mathrm{In}})}\frac{\left(W_{\mathrm{r,Sn}} - 1\right)}{(W_{\mathrm{Sn}} - 1)} \\ &= (W-1)\frac{(W - W_{\mathrm{Sn}})}{(W_{\mathrm{In}} - W_{\mathrm{Sn}})}\frac{1}{S_{\mathrm{In}}} + (W-1)\frac{(W - W_{\mathrm{In}})}{(W_{\mathrm{Sn}} - W_{\mathrm{In}})}\frac{1}{S_{\mathrm{Sn}}} \end{aligned} \tag{12}$$

Note that this can be rearranged as

$$\frac{1}{S} = \frac{1}{S_{\mathrm{In}}}\frac{(W - W_{\mathrm{Sn}})}{(W_{\mathrm{In}} - W_{\mathrm{Sn}})} + \frac{1}{S_{\mathrm{Sn}}}\frac{(W - W_{\mathrm{In}})}{(W_{\mathrm{Sn}} - W_{\mathrm{In}})} \tag{13}$$

so that a quadratic interpolation in W_{r} values is equivalent to a linear interpolation in 1/S values (which is very close to a straight line on Figure 1). The difference in slope between two interpolations corresponds to the difference in S values when the lines are extrapolated to W =1. Note that the equation for other quadratic interpolations can be obtained simply by replacing the subscripts.

The derivative of (12) is

$$\frac{d\,{}^{\mathrm{Sn}}W_{\mathrm{r}}(W)}{dW} = -\frac{(W - W_{\mathrm{Sn}})}{(W_{\mathrm{In}} - W_{\mathrm{Sn}})}\frac{1}{S_{\mathrm{In}}} - \frac{(W - W_{\mathrm{In}})}{(W_{\mathrm{Sn}} - W_{\mathrm{In}})}\frac{1}{S_{\mathrm{Sn}}} + (W-1)(\text{...other terms}) \tag{13}$$

which at the triple point of water (W = 1) simplifies to

$$\left.\frac{d^{Sn}W_{\mathrm{r}}}{dW}\right|_{W=1} = \frac{1}{S_{\mathrm{In}}} + \frac{W_{\mathrm{In}}-1}{W_{\mathrm{In}}-W_{\mathrm{Sn}}}\left(\frac{1}{S_{\mathrm{In}}}-\frac{1}{S_{\mathrm{Sn}}}\right). \tag{14}$$

Note that derivative simplifies to that for the linear water-indium interpolation if the S_i values for the indium and tin fixed points are the same. The derivative of the argon-water interpolating equation at the triple point of water has a very similar form:

$$\left.\frac{d^{Ar}W_{\mathrm{r}}}{dW}\right|_{W=1} = \frac{1}{S_{\mathrm{Hg}}} + \frac{\ln W_{\mathrm{Hg}}}{\ln W_{\mathrm{Hg}}-\ln W_{\mathrm{Ar}}}\left(\frac{1}{S_{\mathrm{Ar}}}-\frac{1}{S_{\mathrm{Hg}}}\right) \tag{15}$$

Again we can see the important of the S_i values. Most importantly, the magnitude of the discontinuity between different interpolating equations depends on the differences between the S_i values. For example, the difference in slope between the argon-water and the water-tin interpolating equations is

$$\left.\frac{d^{Ar}W}{dW}\right|_{W=1} - \left.\frac{d^{Sn}W_{\mathrm{r}}}{dW}\right|_{W=1} = \left(\frac{1}{S_{\mathrm{Hg}}}-\frac{1}{S_{\mathrm{In}}}\right) + \frac{\ln W_{\mathrm{Hg}}}{\ln W_{\mathrm{Hg}}-\ln W_{\mathrm{Ar}}}\left(\frac{1}{S_{\mathrm{Ar}}}-\frac{1}{S_{\mathrm{Hg}}}\right) - \frac{W_{\mathrm{In}}-1}{W_{\mathrm{In}}-W_{\mathrm{Sn}}}\left(\frac{1}{S_{\mathrm{In}}}-\frac{1}{S_{\mathrm{Sn}}}\right). \tag{16}$$

Note particularly, that if all the S_i values are the same then there is no discontinuity.

Another interesting observation is that since $S_i = \left(W_i - 1\right)/\left(W_{\mathrm{r},i} - 1\right)$, the limit of this function as $W \rightarrow 1$ is the reciprocal of the derivative of interest. Therefore, intersections of the interpolation equations with the $W_{\mathrm{r}} = 1$ axis in Figure 1 directly measure the slope dW/dW_{r}, and intersection of the interpolations with the $W_{\mathrm{r}} = 1$ axis, in Figure1, gives a pictorial representation of the slopes at the TPW. The discontinuities are evident from the different points of intersection with $W_{\mathrm{r}} = 1$.

4. Observations on ITS-90 scale artefacts

At least three ITS-90 scale defects are apparent in Figure 1:

(1) There is a large drop in the S_i values between those above and those below $W = 1$.

This observation affirms Richard's (and others) observations on the existence of the discontinuity. Note that the structure of ITS-90 guarantees the existence of discontinuities: what we are taking about here is an observation of discontinuities at 0.01 ºC that are, on average, biased away from zero, and much larger than the typical variations in slope observed elsewhere in the scale.

The origin of the discontinuity at 0.01 ºC is the use of two different SPRTs to establish the values for the reference resistance ratios used in ITS-90. While the two thermometers where very similar they were not identical, and hence the set of reference resistance ratios below 0.01 ºC are not entirely consistent with the reference resistance ratios assigned above 0.01 ºC.

(2) The S_i values for the mercury point seem high in comparison to those for the argon point.

I have had a quick look back through the CCT working documents but have been unable to find anything definite about the assignment of the $W_{\mathrm{r,Hg}}$ value. It is possible that this was tweaked (possibly in the wrong direction) to minimise SRI. Drs Hill and Rusby may be able to recall what was done.

(3) It is apparent that there is experimental noise (either due to measurement error or real differences between SPRTs) in the $W_{\mathrm{r},i}$ values.

The same phenomena presumably affected the two thermometers used to establish the reference resistance ratios, and therefore there is a small random component to the reference resistance ratio values assigned by ITS-90. This effect ensures that discontinuities occur where every subrange terminates.

References

[1] White D.R., Strouse G.F., Observations on sub-range inconsistency in the SPRT interpolations of ITS-90, *Metrologia*, 2009, **46**, 101-108